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(η^6-ARENE)TRICARBONYLCHROMIUM COMPLEXES IN ORGANIC SYNTHESIS: STEREOSELECTIVE ALKYLATION AT BENZYLIC POSITION OF (η^6-ARENE)TRICARBONYLCHROMIUM

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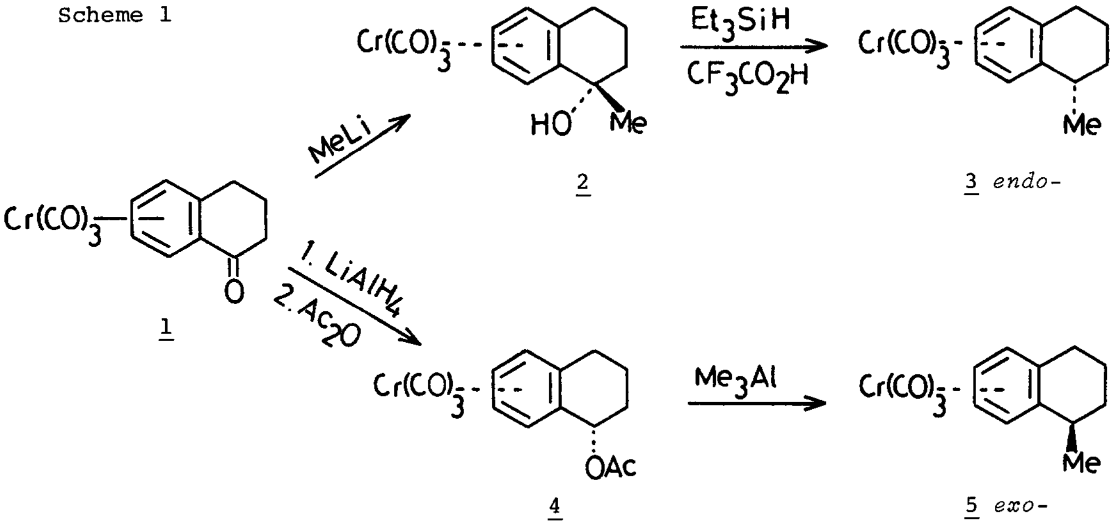
Summary: Benzylic acetates and the corresponding free alcohols of (η^6-arene) tricarbonylchromium complexes are alkylated stereoselectively with trialkylaluminum or diethylzinc to give *exo*-alkyl chromium complexes in high yield.

(η^6-Arene)tricarbonylchromium complexes, easily obtained from the arene and $Cr(CO)_6$, have some characteristic properties due to the strong electron-withdrawing ability and the steric bulkiness of $Cr(CO)_3$ group, and their significant applications in organic synthesis have been developed1). One consequence of the complexation by $Cr(CO)_3$ is the increased stability of the benzylic carbocations, which could be trapped with nucleophiles such as ROH, H_2O, RSH and RCN2). While considerable attention has been centered upon the magnitude and possible modes of this stabilization, the potential utility of these cations in carbon-carbon bond formation is very few3). We now wish to report the stereoselective alkyl substitution at the benzylic position of (arene)tricarbonylchromium complexes with trialkylaluminum or dialkylzinc.

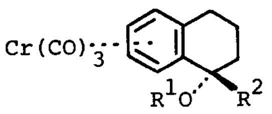
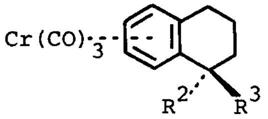
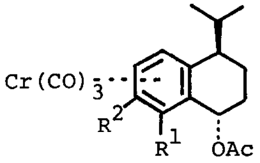
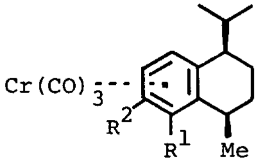
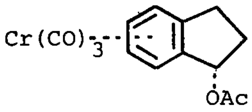
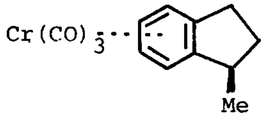
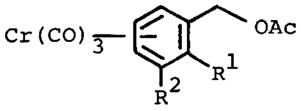
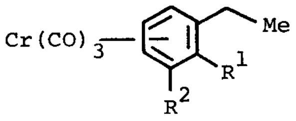
It is well documentated that two possible diastereomeric chromium complexes, *endo*- and *exo*-isomers, are obtained as a mixture by direct complexation of 1-alkylindane or 1-alkyltetralin with $Cr(CO)_6$, and the ratio of the isomers depends upon the steric effect and the nature of the substituents4). However, it could be possible to obtain either *endo*- or *exo*-isomers from a common α-tetralone or α-indanone stereoselectively, based on the above two factors (steric bulkiness and stability of carbocation of (arene)chromium complexes). For example, a complex 2 obtained from (α-tetralone)tricarbonyl chromium 1 and MeLi, afforded an (1-*endo*-methyltetralin)tricarbonylchromium (3, mp 84 °C) by ionic hydrogenolysis5) with an excess of triethylsilane and trifloroacetic acid via stereoselective *exo*-hydride displacement6). On the other hand, an *endo*-acetate complex 4 was converted into an (1-*exo*-methyltetralin)-tricarbonylchromium (5, mp 94 °C) via *exo*-methyl attack to the carbocation by treatment with Me$_3$Al7) (Scheme 1).

Scheme 1

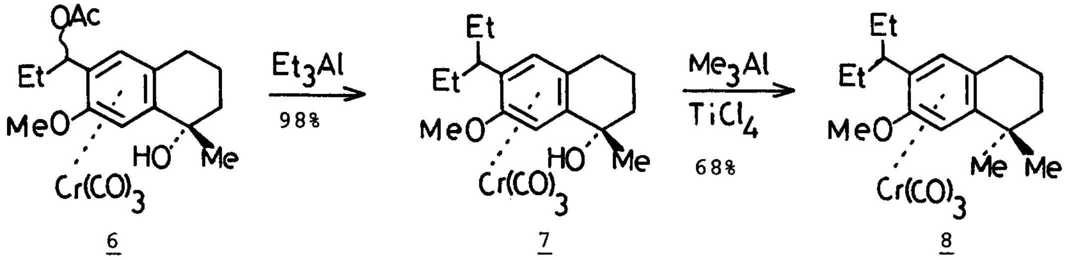


Other chromium complexes possessing a benzylic acetoxyl group were similarly alkylated with trialkylaluminum to give *exo*-alkyl complexes (Table). The (1-*exo*-methyl-4-*exo*-isopropyl-methoxytetralin)chromium complexes (13 and 15) are key intermediates for the stereoselective synthesis of cadinane sesquiterpenoid, *cis*-7 or 8-hydroxycalamenene. The free benzylic hydroxyl group could not be replaced by Me$_3$Al alone, but is substituted smoothly at room temperature in the presence of 1 eq of TiCl$_4$ (entries 3∿4). In the reaction with Et$_2$Zn, both the acetate complex 4 and the corresponding free alcohol complex 10 gave the *exo*-ethyl complex 9 only in the presence of TiCl$_4$ (entries 5∿6). This type of substitution is also succesful even in primary acetate complexes (entries 10∿11). Two different alkyl groups could be introduced stepwise at the different benzylic positions depending upon the reaction conditions. Thus, the secondary benzylic acetoxyl group of a complex 68) was replaced by Et$_3$Al alone at first to give a complex 7 and then tertiay hydroxyl group was substituted by the reaction with Me_3Al in the presence of $TiCl_4$ to afford a chromium complex 8 in good yield (Scheme 2).

Table

entry	complexes		reagents (R^3)	products		yield
						
1	R^1=Ac, R^2=H	4	Me_3Al	R^2=H, R^3=Me	5	99
2	R^1=Ac, R^2=H	4	Et_3Al	R^2=H, R^3=Et	9	60
3	R^1=R^2=H	10	Me_3Al, $TiCl_4$	R^2=H, R^3=Me	5	60
4	R^1=H, R^2=Me	2	Me_3Al, $TiCl_4$	R^2=R^3=Me	11	92
5	R^1=Ac, R^2=H	4	Et_2Zn, $TiCl_4$	R^2=H, R^3=Et	9	62
6	R^1=R^2=H	10	Et_2Zn, $TiCl_4$	R^2=H, R^3=Et	9	60
						
7	R^1=H, R^2=OMe	12	Me_3Al	R^1=H, R^2=OMe	13	95
8	R^1=OMe, R^2=H	14	Me_3Al	R^1=OMe, R^2=H	15	99
9		16	Me_3Al		17	53
						
10	R^1=H, R^2=OMe	18	Me_3Al	R^1=H, R^2=OMe	19	96
11	R^1=OMe, R^2=H	20	Me_3Al	R^1=OMe, R^2=H	21	95

Scheme 2



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References and Notes

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2) [a]S. Top, A. Meyer, and G. Jaouen, Tetrahedron Lett., 3537 (1979); [b]S. Top, and G. Jaouen, J. Chem. Soc., Chem. Commun., 224 (1979); [c]Idem, J. Org. Chem., 46, 78 (1981); [d]S. G. Davies, N. J. Holman, C. A. Laughton, and B. E. Mobbs, J. Chem. Soc., Chem. Commun., 1316 (1983).

3) To our knowlege, only one example for the C-C bond formation has been reported by use of enol silyl ethers and secondary benzylacetate complexes: M. T. Reetz and M. Sauerwald, Tetrahedron Lett., 24, 2387 (1983).

4) B. E. F. Gracey, W. R. Jackson, W. B. Jennings, and T. R. B. Mitchell, J. Chem. Soc., (B), 1204 (1969) and references cited therein.

5) [a]D. N. Kursanov, Z. N. Parnes, and N. M. Lion, Synthesis, 633 (1974); [b]M. Uemura, K. Isobe, K. Take, and Y. Hayashi, J. Org. Chem., 48, 3855 (1983).

6) Electrophilic or nucleophilic attack at the reactive center always occurs stereoselectively in an *exo*-fashion: A. Meyer and O. Hofer, J. Am. Chem. Soc., 102, 4410 (1980).

7) A typical experimental procedure is as follows. Me_3Al (4.2ml, 10% w/w in hexane, 3.6mmol) was added to a solution of the complex 4 (326mg, 1mmol) in dry CH_2Cl_2 (15ml) under argon at $-78^{\circ}C$. The mixture was stirred for 30min, and then for 1h at $0^{\circ}C$. After addition of H_2O, the mixture was extracted with CH_2Cl_2, and the extract was evaporated to give the complex 5 (282mg) after purification by SiO_2 chromatography. The complex 5 and other new complexes gave correct combustional analyses and satisfactory spectral data.

8) The complex 6 was prepared from a (7-methoxy-1-tetralone)tricarbonylchromium as following reactions; 1) MeLi, 2) n-BuLi/TMEDA, 3) EtCHO, 4) Ac_2O/pyridine Directed regioselective lithiation of (7-methoxy-1-tetralol)chromium complex; M. Uemura, N. Nishikawa, K. Take, M. Ohnishi, K. Hirotsu, T. Higuchi, and Y. Hayashi, J. Org. Chem., 48, 2349 (1983).

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