# Chromium Trichloride Tetrahydrofuranate[1]

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The reaction of anhydrous chromium trichloride and phenylmagnesium bromide in ether[2] or in tetrahydrofuran[3] is necessarily a heterogeneous one owing to the extreme insolubility of this metallic halide in organic solvents. Inorganic salts of chromium are in fact generally insoluble in all nonhydroxylic solvents; and this property presents difficulties in promoting their reactions in organic solvents with organic reagents. We have now found that the trichloride may be made soluble by complexing it with tetrahydrofuran and that its reactions with Grignard reagents proceed rapidly, quantitatively, and homogeneously in this form.

The conversion of anhydrous chromium trichloride into its tetrahydrofuranate is achieved by the continuous extraction with anhydrous tetrahydrofuran of its solid form admixed with catalytic amounts of zinc dust. In this manner the halide is quantitatively extracted by the solvent from which the violet tetrahydrofuranate is crystallized. The zinc metal which is recovered unchanged is considered to behave as a reducing agent, solubilizing chromium in its divalent form, followed by subsequent reduction itself and concurrent formation of $CrCl_3(THF)_3$.[4] The coordinating tetrahydrofuran molecules are very tightly bound in the complex, for they are not lost even upon heating of the complex to 100° at 20 mm., and the tetrahydrofuranate may be kept in the open air several hours without appreciable hydrolysis, since the crystals are only slightly hygroscopic and deliquesce quite slowly to a green hydrate. Consequently, as a reagent it may be stored indefinitely without decomposition so long as it is kept dry.

## EXPERIMENTAL

*Chromium trichloride tri-tetrahydrofuranate.* The tetrahydrofuran (Mathieson, Coleman and Bell, b.p. 64–66°) used in this preparation was purified and dried by refluxing over sodium ribbon with fresh ribbon being added until new ribbon maintained a clean surface after 5 hr. of refluxing. Just prior to use the THF was distilled, treated with fresh sodium ribbon and with lithium aluminum hydride, and then redistilled in a stream of dry, oxygen-free nitrogen (GE lamp grade is suitable for this purpose without further drying and/or purification).

Anhydrous chromium trichloride (Fisher), 12.21 g., mixed with 0.15 g. of zinc dust, is placed in the thimble of a Soxhlet extraction apparatus and then extracted overnight with 140 ml. of boiling THF or until no further color is observable in the cycling liquid (10–15 hr.). After complete extraction only zinc dust remains in the extraction thimble, while the pot flask contains the solution of the tetrahydrofuranate (2.8 g./100 ml. of hot THF) together with the crystalline chromium trichloride tri-tetrahydrofuranate which has crystallized during extraction. Concentration, cooling, and filtration are employed to isolate the crystalline form in essentially quantitative yield.

*Anal.* Calcd. for $CrCl_3(C_4H_8O)_3$: Cr, 13.88; Cl, 28.39. Found: Cr, 13.42; Cl, 28.57, 28.19.

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[1] Paper VI, "$\pi$-Complexes of the Transition Metals"; Paper V, H. H. Zeiss and W. Herwig, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

[2] H. H. Zeiss and M. Tsutsui, *J. Am. Chem. Soc.*, **79**, 3062 (1957).

[3] W. Herwig and H. H. Zeiss, *J. Am. Chem. Soc.*, **79**, 5959 (1957).

[4] This phenomenon has been observed previously in that chromous chloride will cause the trichloride to dissolve in ether: N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Oxford Univ. Press, New York, N. Y., 1950, p. 1012.

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# Preparation of a New Class of Steroids with Unnatural Configuration. The 19-Nor-5α,10α Series

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There are four possible steric arrangements of the A/B rings of the 19-nordihydrosteroid nucleus (the *trans-syn-trans* conformation requires a boat form for ring B), all other centers of asymmetry being kept constant. The allo configurational series ($5\alpha,10\beta$) was reported by Bowers, Ringold, and Dorfman[1] while the normal series ($5\beta,10\beta$) was described recently from this Laboratory.[2]

This communication reports the synthesis of a third and hitherto unknown series of 19-norsteroids, and evidence is presented which permits assignment of structure and classification as 19-nor-$5\alpha,10\alpha$-dihydrosteroids.

Hydrogenation of $17\alpha$-ethinyl- or $17\alpha$-ethyl-$17\beta$-estradiol with ruthenium dioxide catalyst at elevated pressures afforded a crystalline product, $17\alpha$-ethyl-$5\alpha,10\alpha$-estrane-$3\beta,17\beta$-diol (Ia) (m.p. 143–145°; $[\alpha]_D^{25}$ −20.9° ($CHCl_3$). Found for $C_{20}H_{34}O_2$: C, 78.11; H, 11.27) in excellent yield. Oxidation of this diol with chromic anhydride-pyridine gave $17\alpha$-ethyl-$5\alpha,10\alpha$-estran-$17\beta$-ol-3-one (IIa) (m.p. 205–207°; $[\alpha]_D^{25}$ −66.4°. Found for $C_{20}H_{32}O_2$: C, 78.67; H, 10.99).[3] Sodium and pro-

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[1] A. Bowers, H. J. Ringold, and R. I. Dorfman, *J. Am. Chem. Soc.*, **79**, 4556 (1957).

[2] R. T. Rapala and E. Farkas, *J. Am. Chem. Soc.*, **80**, 1008 (1958).

[3] All melting points are uncorrected. We gratefully acknowledge valuable technical assistance by Messr. W. Scanlon, hydrogenation experiments; Messrs. G. M. Maciak, W. L. Brown, and H. L. Hunter, elemental analysis. All rotations are done in methanol unless otherwise specified.