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Chromyl(VI) Hexafluoroisopropoxide, $CrO_2[OCH(CF_3)_2]_2$

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The oxidation of alcohols by certain transition metal oxo-species in high oxidation states, including CrO_3 and $[Cr_2O_7]^{2-}$, has long been known [1]. As a consequence, the metal is reduced and the possible mechanism [2] for such a reduction has been proposed as hydride abstraction from the alcohol/–OR moiety. Reaction of CrO_2Cl_2 with ethanol and isopropanol [3] has been shown to give green products, which may very likely be the chromium(III) rather than the dioxochromium(VI) derivatives, since the former are usually green and the latter are yellow, red or brown [4]. The synthetic strategy to stabilise chromyl(VI) alkoxide, therefore, lies in checking the hydride abstraction from alcohol and this can be envisaged by substituting a strong electron-withdrawing moiety in the alkyl group of the alcohol. Success in stabilising chromyl(VI) alkoxide has been achieved by using hexafluoroisopropanol.

Reaction of CrO_2Cl_2 with $LiOCH(CF_3)_2$ in a 1:2 molar ratio yielded a dark brown solid, which on analysis was found to be $CrO_2[OCH(CF_3)_2]_2$. This compound is diamagnetic and shows in its IR spectrum $\nu(C-O)$ [5] at 1100 cm^{-1} and asymmetric and symmetric Cr=O stretching frequencies [4, 6] at 1030 and 980 cm^{-1}, respectively. Its ^{19}F NMR spectrum shows a sharp doublet at 75 ppm as compared to 78 ppm for the pure alcohol.

Experimental

All preparations were carried out in oxygen-free dry nitrogen.

Dioxo-bis(1,1,1,3,3,3-hexafluoroisopropoxy) Chromium(VI)

A mixture of CrO_2Cl_2 in dry CCl_4 (10 cm^3) and lithium (1,1,1,3,3,3-hexafluoroisopropoxide) in a 1:2 molar ratio was heated under reflux for *ca.* 5 h and CCl_4 was pumped off. Ether (3 × 20 cm^3) was added to precipitate LiCl and the resulting suspension filtered to give a reddish brown filtrate which on evaporation gave a dark brown solid, melting point >240 °C. *Anal.* Calc. for $CrO_2(OCH(CF_3)_2)_2$: C, 17.2; H, 0.47; Cr, 12.44; F, 54.74. Found: C, 16.5; H, 0.57; Cr, 12.5; F, 53.9%. IR: 1380, 1330, 1300, 1270, 1225, 1192, 1100, 1030, 980, 810, 630 cm^{-1}.

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