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REACTIONS OF FREE RADICALS WITH MONOETHYLDICHLOROCHROMIUM(III) TRIS(TETRAHYDROFURANATE)

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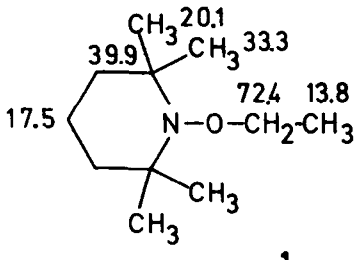
Summary: σ-Ethyl-chromium(III)dichloride · 3 THF reacts with free radicals by formation of a transient paramagnetic complex which decomposes giving the combination product of alkyl ligand and radical.

The preparation and chemistry of σ-alkylchromium complexes has been investigated for a number of years 1,2). While most of the work was concerned with the formation and the decomposition of the complexes their chemistry has not been studied extensively. We wish to report on the interaction of σ-bonded mono(organo)chromium(III)compounds with free radicals.

ESR-spectroscopic monitoring of the reaction of mono(ethyl)chromium(III) dichloride 3) in THF/Hexane 1:1 below 0°C with equimolar amounts of 2.2.6.6-tetramethylpiperidine nitroxide leads to the immediate disappearance of the 1:1:1-triplet of the nitroxide radical and to the formation of a strong singlet(linewidth = 1.6 mT, g-value = 1.982). This ESR-spectrum, which is in agreement with literature values on chromium(IV) ESR-data 4), remains unchanged at -60°C over longer periods of time. At +10°C it decays with a half life of 7.4 min. by a first order process ($k = 2 \times 10^{-3}\ s^{-1}$). In order to identify the products of this reaction 1.3 mmol of the ethylchromium(III)complex in THF was treated with an equimolar amount of the nitroxide in THF at room temperature. Within a few minutes the formerly green solution turns brown. $CrCl_2$ · THF precipitates from the THF solution and can be isolated. Hydrolysis and hexane extraction after 1 hour leads after workup to a compound (yield = 67%) for which elemental analysis and ^{13}C-NMR spectrum (chemical shifts are given in 1, standard TMS) proves the structure of a combination product.



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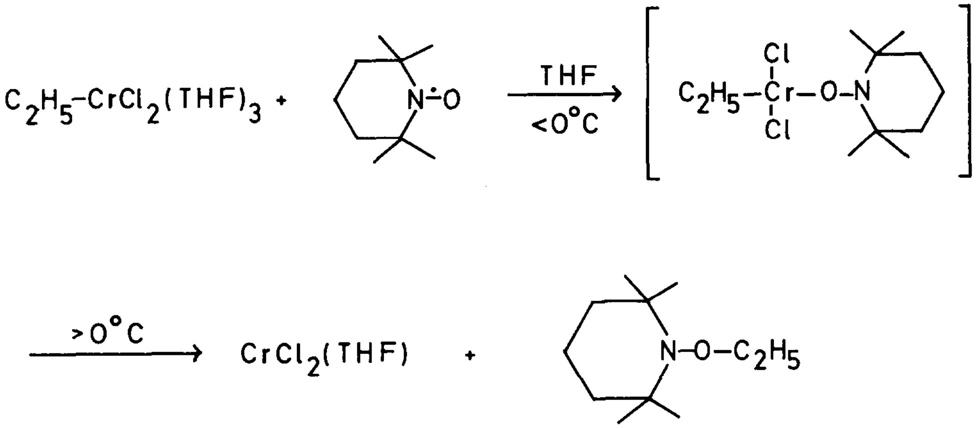
We interpret these results in terms of the following reaction scheme:



The generality of this coupling reaction has been tested in several cases. Thermal decomposition at room temperature of dicyclohexanecarbonylperoxide in the presence of two equivalents of the ethylchromiumdichloride complex leads to the coupling of cyclohexyl radical with ethyl in 40% yield. Similarly, reaction of the chromium complex with triphenylmethyl radicals, formed by dissociation of its dimer, gives 1.1.1-triphenylpropane in 74%.

These results are not only important with respect to preparative applications (see following communication) but also with respect to the thermal decomposition of mono-σ-alkylchromium(III)complexes. The exact mechanisms of these latter processes are not known [1,2]. The formation of dimers and disproportionation products has been suggested to occur via radicals or via concerted elimination from binuclear complexes. As the decomposition of monoorganochromium(III) compounds in radical R· and chromous(II) ion is known [5], our results suggest that at least part of the dimers is formed via an organochromium(IV) complex formed by addition of a radical R· to an undecomposed complex R-CrCl$_2$· 3THF. This could explain the fact that the ratio of dimers to disproportionation products differs from those for true free radical reactions.

Further work on these reactions is in progress.

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