NMR spectroscopic evidence for chromium(VI) alkoxides with α-hydrogen atoms

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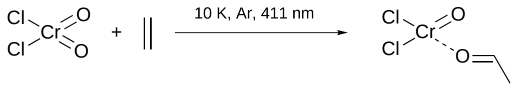
Selective insertion of epoxides into one Cr–Cl bond of chromyl chloride at −50 °C enabled, for the first time, the spectroscopic identification of Cr^{VI} alkoxides with α-hydrogen atoms.

For quite some time alkene oxidation with chromyl chloride seemed to proceed completely unspecifically and uncontrollably.[1] In 1977 Sharpless *et al.* made an attempt to explain the occurrence of the various products and the stereochemistry involved *via* several intermediates[2] which subsequently aggregate to the Etard complex and none of which have ever been characterised.

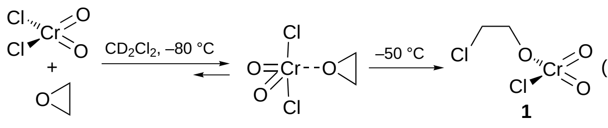
Recently, with the aid of matrix isolation an alkene oxidation by chromyl chloride could be stopped before aggregation and the species $O{=}CrCl_2\cdots O{=}CHCH_3$ [eqn. (1)] was identified.[3]



(1)

This finding could provide an explanation for the isolation of carbonyl compounds after such reactions, which had previously been understood as a result of the rearrangement of chlorohydrins and epoxides in solution.[1]

Formation of this complex could be considered *via* photolysis of the intermediate $O{=}CrCl_2\cdots\overline{OCH_2}CH_2$ stimulating an investigation concerning the behaviour of ethylene oxide in the presence of Lewis acids at low temperatures. Since $O{=}CrCl_2$ is not available on a preparative scale, in search of an appropriate reagent which could model some of the properties of $O{=}CrCl_2$, the initial starting material, CrO_2Cl_2, was studied. After co-condensation of this reagent with 1 equiv. of ethylene oxide and CD_2Cl_2 in an NMR tube and flame-sealing the sample was investigated at −80 °C. ^1H NMR spectra (Fig. 1) showed that ethylene oxide co-ordinates to CrO_2Cl_2, as indicated by a broad resonance at δ 3.29 for the ethylene oxide protons.† This signal remains at this position if a second equiv. of ethylene oxide is added meaning that CrO_2Cl_2 is capable of co-ordinating up to two epoxide molecules. Consequently the complex shown in eqn. (2) must be in equilibrium not only with free CrO_2Cl_2 but



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(2)

also with $CrO_2Cl_2{\cdot}2OC_2H_4$. Correspondingly, if 4 equiv. of ethylene oxide are reacted with CrO_2Cl_2 a signal at δ 3.01, intermediate between free and co-ordinated oxirane, is observed. Photolysis at this stage resulted in C–H activation and formation of paramagnetic compounds. However, warming of a 1:1 sample to −50 °C triggered a cleavage reaction of the three-membered ring[4] by one Cl ligand of CrO_2Cl_2 producing the species $O_2Cr(OCH_2CH_2Cl)Cl$ **1**. After 60 min the yield of **1** amounts to 75%, however, at this stage the decomposition rate of **1** becomes faster than its formation.

Dark red **1** has been characterised by ^1H, ^{13}C (135° DEPT), $^1H/^{13}C$-HMQC and $^1H/^1H$-COSY NMR spectra showing two coupling CH_2 groups‡ both of which appear in the characteristic regions for the proposed connectivity. In addition ^{17}O NMR data of concentrated samples were recorded: the initial signal of the CrO_2 group of the CrO_2Cl_2–oxirane complex (one broad resonance at δ 1476) decreased at −50 °C in favour of a new signal for the terminal oxygens in **1** at δ 1429 indicating that the CrO_2 group has been preserved. Signals for the oxirane and alkoxide oxygens could not be detected in accordance with the results of investigations concerning molybdate esters.[5] Concentration dependent experiments in the presence of a standard (CH_2Cl_2) confirmed that only 1 equiv. of ethylene oxide per Cr centre is consumed during the formation of **1** and that accordingly ethylene oxide inserts into only one Cr–Cl bond excluding the formation of the bis(2-chloroethyl) chromate ester. Instead, increasing the initial concentration of the oxirane decreases the lifetime of **1**, which decomposes to paramagnetic dark brown compounds, so terminating the NMR experiments. These species, small amounts of which are constantly generated at −50 °C at any ethylene oxide concentration, can explain the continuous broadening of the signal of ethylene oxide and its shifting to higher field (Fig. 1): ethylene oxide equilibrating rapidly between its free state and complexation to CrO_2Cl_2 and **1** also binds reversibly to the paramagnetic compounds and therefore the averaged signal observed in the experiment is increasingly broadened with time. In $CFCl_3$ the paramagnetic complexes precipitate as brown solids and accordingly the ethylene oxide signal does not shift or broaden significantly. The positive results after replacement of CD_2Cl_2 additionally rule out its participation in the reaction sequence leading to **1**.

1 is contaminated by only one other compound, **2** (*ca.* 8% in the experiment shown in Fig. 1), whose identification proved difficult because of its low concentration, limited stability and

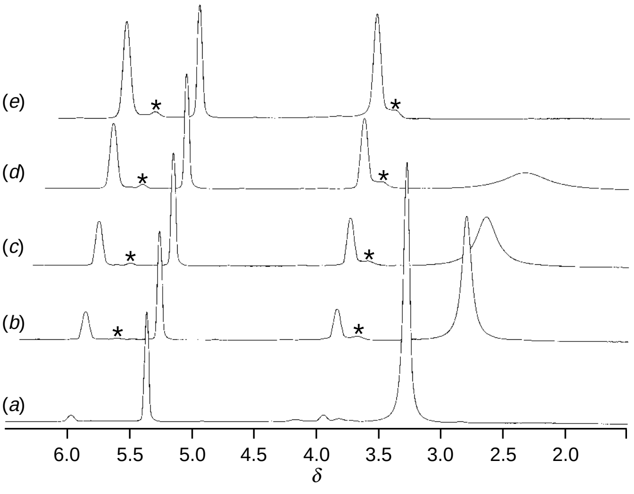
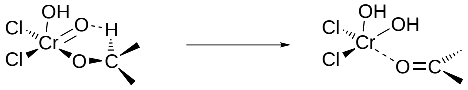


Fig. 1 ^1H NMR spectra of a mixture of 0.8 mmol CrO_2Cl_2 and 0.8 mmol of ethylene oxide in CD_2Cl_2 (*a*) at −80 °C and after annealing to −50 °C for (*b*) 10 min, (*c*) 20 min, (*d*) 40 min and (*e*) 60 min. The signals marked with an asterisk belong to **2**.

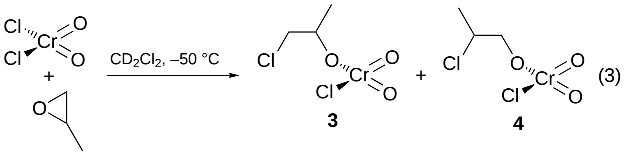
considerable linewidths of its signals thwarting all attempts to record COSY spectra. Its ^{1}H and ^{13}C NMR data may be interpreted in terms of the compound $O_2Cr(Cl)OCH_2CH_2OCH_2CH_2Cl$ being formed by insertion of two ethylene oxide molecules into one Cr–Cl bond. This is supported by the fact that $FeCl_3$ has been found to react with ethylene oxide to give uncharacterised chloroferric alkoxides producing chloroethanol and 2-(2-chloroethoxy)ethanol upon hydrolysis.[6] However, due to the insufficient spectroscopic data the assignment of **2** is speculative.



Scheme 1

Compound **1** is remarkable because it is the first Cr^{VI} alkoxide with α-hydrogens whose existence has been proved spectroscopically.§ It is well known that Cr^{VI} compounds oxidise primary and secondary alcohols to carbonyl compounds[8] and recent DFT calculations by Deng and Ziegler[10] have shown that the key step in CrO_2Cl_2 oxidations is probably that shown in Scheme 1. While chromate esters of tertiary alcohols[11] are protected against this decomposition route the activation of α-hydrogens by terminal Cr=O groups is possible for **1** so that its thermal sensitivity (decomp. within 15 min at −30 °C) is not a surprise. However, the smooth synthesis presented above which can be performed at low temperatures without simultaneous formation of by-products allows its NMR spectroscopic characterisation. Attempts to isolate **1** and **2** at −50 °C by removal of all volatiles led to a brown glass, whose hydrolysis yielded, as expected, 2-chloroethanol and chloroacetaldehyde contaminated by small amounts of compounds of unknown composition, some of which were identical with the chromyl chloride oxidation products of 2-(2-chloroethoxy)-ethanol, supporting the assignment of **2**. When the brown glass is annealed to room temp. in the absence of any reactant a heterogeneous decomposition product is obtained in which the organic oxidation products remain coordinated to the chromium centres as they do in the Etard complex.[12] Accordingly its IR spectrum is dominated by strong bands at 3301 [ν(OH)], 1640/1570/1430 [ν(C=O)] and 1066 cm^{-1} [ν(C–O)].

Surprisingly, when propylene oxide was reacted with CrO_2Cl_2 at −50 °C both possible regioisomers[12] were found in a close to 1 : 1 ratio [eqn. (3)]. A similar lack of selectivity has been found *e.g.* in epoxide cleavages using $VCl_3{\cdot}3thf$.[13] The reaction mechanism and the stereochemistry involved in epoxide opening by CrO_2Cl_2 are under current investigation. Further research also concerns the expansion of this novel route yielding oxochromium(VI) alkoxides to the syntheses of stable candidates of this class of compounds, *i.e.* those eluding α-hydrogens, which find application as useful oxidation reagents.[10]



3 **4** (3)

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Footnotes and References

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† Free ethylene oxide shows a singlet at δ 2.58.

‡ Owing to the linewidths of the signals no coupling information could be deduced from the COSY experiments. In Fig. 1 no coupling is resolved, in other experiments, however, a triplet structure for the two signals became obvious. ^{1}H NMR (200 MHz, CD_2Cl_2, −50 °C, $SiMe_4$): δ_H 5.96 [2 H, br t, ^3J(HH) 4.8 Hz, OCH_2], 3.95 [2 H, br t, ^3J(HH) 4.8 Hz, $ClCH_2$]; ^{13}C NMR (200 MHz, CD_2Cl_2, −50 °C, $SiMe_4$): δ_C 94.22 (OCH_2), 46.06 ($ClCH_2$).

§ Chada *et al.*[7] claim to have prepared oligomers of $O_2Cr(OCH_2CH_2Cl)_2$ (said to show just one singlet by ^{1}H NMR) by refluxing CrO_2Cl_2 with the corresponding alcohol in CCl_4 and **1** (neither analytical nor spectroscopic data are given) by treatment of CrO_2Cl_2 with $Li(OCH_2CH_2Cl)$ in CCl_4. Since primary and secondary alcohols are oxidised by Cr^{VI} compounds at room temp.[8] it did not surprise us that these rather drastic conditions in our hands did not yield the compounds mentioned above rather than green solids with strong ν(C=O) bands in the IR spectra. An NMR spectroscopic investigation showed that $HOCH_2CH_2Cl$ reacts with CrO_2Cl_2 already at temperatures below −80 °C producing paramagnetic species. Westheimer *et al.*[9] reported the *in situ* preparation of bisisopropyl chromate from CrO_3 and Pr^iOH which was characterised by elemental analyses of its decomposition products.

¶ **3**: δ_H 6.14 (1 H, br m, OCH), 3.82 (2 H, br m), $ClCH_2$), 1.68 [3 H, d, ^3J(HH) 5.20 Hz, CH_3]; δ_C 99.38 (OCH), 49.43 ($ClCH_2$), 21.41 (CH_3). **4**: δ_H 5.83 [2 H, d, ^3J(HH) 4.8 Hz, OCH_2], 4.37 (1 H, m, ClCH), 1.57 [3 H, d, ^3J(HH) 5.20 Hz, CH_3]; δ_C 98.14 (OCH_2), 57.69 (ClCH), 21.35 (CH_3).

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