

VICINAL ACETOXYCHLORINATION OF OLEFINS BY CHROMYL CHLORIDE IN  
ACETYL CHLORIDE

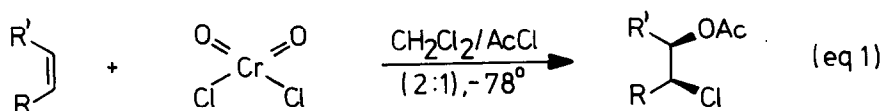
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Chromyl chloride oxidations of olefins are notorious for producing complex mixtures of products.<sup>1-6</sup> Chlorohydrins, chloroketones, epoxides, and dichlorides are among the products which have been found. We have reported<sup>5</sup> that chloroketones are formed selectively when the oxidations are carried out in acetone. We have also found<sup>6</sup> that chlorohydrins and epoxides are the major products when the oxidations are performed at low temperature in methylene chloride. A remarkable aspect of these low temperature oxidations was the discovery that the chlorohydrins are those resulting from highly stereoselective cis-addition of the elements of OH and Cl across the olefinic linkage. To account for these unusual observations a new mechanism involving organometallic intermediates (Cr-C  $\sigma$ -bonds) was proposed.<sup>6</sup>

We have now found another modification which leads to highly preferential formation of a single useful product. When chromyl chloride oxidations of olefins are performed in the presence of acetyl chloride, vicinal chloroacetates are produced in good yields.

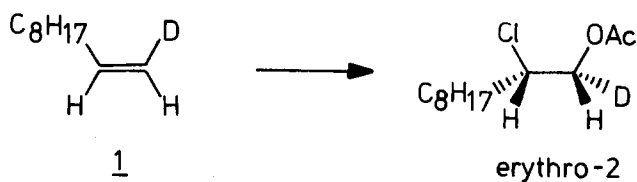


The reactions were performed at  $-78^\circ$  using methylene chloride/acetyl chloride (2:1) as solvent. The following procedure is representative: 1-Hexene (2.52 g, 30 mmol) was added to a stirred solution of chromyl chloride (4.96 g, 32 mmol) in methylene chloride (100 ml) and acetyl chloride (50 ml) at  $-78^\circ$ . The reaction mixture was stirred at  $-78^\circ$  for 1.5 h then the temperature was raised and the stirring was continued at room temperature for 1.5 h. After cooling to  $0^\circ$ , 3 ml of dimethyl sulfide was added. The purple solution was concentrated to dryness under reduced pressure. Water (100 ml) and ether (50 ml) were added and the

mixture stirred until all solid material had dissolved. The aqueous phase was extracted with ether. The combined organic phases were washed with  $\text{NaHCO}_3$  solution and dried ( $\text{MgSO}_4$ ). The solvent was removed under reduced pressure and the residue was distilled in vacuo to give 4.11 g (77% yield) of a 5:1 mixture (glc) of 2-chloro-1-hexyl acetate and 1-chloro-2-hexyl acetate: bp = 68-72° (3 mm) (lit<sup>7</sup> bp = 93-99° (12 mm) ).

The results in Table 1 show that yields of chloroacetates from mono- and 1,2-disubstituted olefins range between 55 and 90%. Unsymmetrical olefins show a high preference for the regioisomer in which the chlorine atom is attached to the more substituted carbon (i.e. formally anti-Markownikoff addition of the elements of  $\text{Cl}^+$  and  $\text{OAc}^-$  across the double bond). Thus in the oxidation of styrene and 2-methyl-1-tridecene only chloroacetate with the acetoxy group at the terminal carbon could be detected.

As shown by the oxidation of (Z)-1-deuterio-1-decene 1,<sup>8</sup> there is a preference for cis-addition of the elements of Cl and OAc. On oxidation the olefin 1



gave the chloroacetate 2.<sup>9</sup> Hydrolysis of 2 and subsequent analysis<sup>6</sup> of the chlorohydrin formed indicated a ratio erythro-2:threo-2 of 4.0:1.0. Similarly, (E)-cyclododecene gave threo-2-chlorocyclododecyl acetate (Table 1). However, (Z)- and (E)-5-decene and cyclohexene gave varying mixtures of erythro- and threo-chloroacetates. Presumably, the isomers resulting from trans-addition of Cl-OAc were due to trans-opening of an epoxide intermediate.<sup>6,10</sup> Epoxides, with the same geometry as the olefin, have been isolated<sup>3,6</sup> in chromyl chloride oxidations of olefins. No epoxides<sup>10</sup> were detected (<1%) under the present reaction conditions, but greater amounts of trans-adducts were formed compared to the related chromyl chloride oxidations where epoxides are more stable to the reaction conditions.<sup>6</sup>

The preference for cis-addition found here for the acetoxychlorination suggests a mechanism, similar to that proposed earlier<sup>6</sup> for chromyl chloride oxidations of olefins, involving chromium-carbon bonds. The chloroacetates are probably formed by cleavage of the chromium oxygen bond in the chromium ester (e.g. 3) by acetyl chloride. This removes the product from the metal, and thereby protects it from over-oxidation.

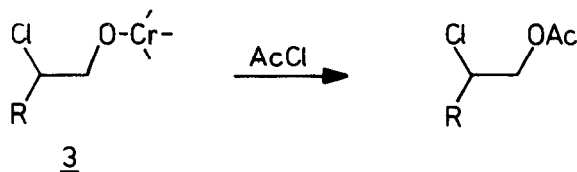


TABLE 1

olefin	total yield of chloroacetate (%)	isomer distribution <sup>b</sup>
1-Hexene	77 <sup>a</sup>	1-acetate:2-acetate = 5.2:1
1-Decene	88 <sup>b</sup>	1-acetate:2-acetate = 5.1:1
( <u>Z</u> )-5-Decene	78 <sup>b</sup>	<u>erythro</u> : <u>threo</u> = 1 :2.0
( <u>E</u> )-5-Decene	64 <sup>a</sup>	<u>erythro</u> : <u>threo</u> = 1 :4.5
Styrene	55 <sup>b</sup>	only C <sub>6</sub> H <sub>5</sub> CH(Cl)CH <sub>2</sub> OAc <sup>c</sup>
( <u>E</u> )-Cyclododecene	56 <sup>b</sup>	<u>threo</u> (>95%)
Cyclohexene	71 <sup>a</sup>	<u>erythro</u> : <u>threo</u> = 1 :2.5
3-Ethyl-3-Octene	44 <sup>a</sup>	4-acetate:3-acetate = 9 :1
2-Methyl-1-tridecene	29 <sup>b</sup>	only C <sub>11</sub> H <sub>23</sub> C(CH <sub>3</sub> )(Cl)CH <sub>2</sub> OAc <sup>c</sup>

a. Isolated yield after distillation. b. Determined by glc using an internal standard. c. The assignment of regioisomers in these cases was made using NMR (CCl<sub>4</sub>, TMS): 2-chloro-2-phenylethylacetate,  $\delta$  = 4.34 (d, CH<sub>2</sub>OAc), 5.0 ppm (t, CHCl); 2-chloro-2-methyl-1-tridecyl acetate,  $\delta$  = 4.15 ppm (s, CH<sub>2</sub>OAc). d. Determined by hydrolysis to the corresponding chlorohydrin, which was analysed by glc (ref 6).

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8. Prepared according to the procedure described by U. G. Wilke and H. Müller, Justus Liebigs Ann. Chem., **618**, 267 (1958).
9. The chloroacetate 2 was purified by preparative TLC (silica gel, ethyl acetate-hexane (1:20) ). In this way the regioisomer 1-chloro-2-decyl acetate was removed.
10. Epoxides were rapidly opened by acetyl chloride under the reaction conditions as shown by a control experiment. Epoxide opening has been shown to account for the trans-adducts formed in related chromyl chloride oxidations of olefins.<sup>6</sup>