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Simple and Selective Method for Aldehydes (RCHO) \rightarrow (E)-Haloalkenes (RCH:CHX) Conversion by means of a Haloform-Chromous Chloride System

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The Takai Olefination: Simple Access to E-Alkenyl **Halides**

CHX₃ (2.0 equiv),
$$R = Alk, alkenyl, Ar$$

$$X = Cl, Br, I$$

$$CrCl2 (6.0 equiv) or CrBr3 (6.0 equiv), LiAlH4 (3.0 equiv)
$$R = Alk, alkenyl, Ar$$

$$X = Cl, Br, I$$

$$Up to 87\% yield$$

$$E/Z up to 95:5$$$$

Selected examples:

87% yield 76% yield 78% yield 55% yield
$$E/Z = 94:6$$
 $E/Z = 89:11$ $E/Z = 89:11$

Br

 $On-Bu$

Competition experiments:

CHI₃ (2.0 equiv)
 $CrCl_2$ (6.0 equiv)
 THF , 0 °C, 1 h

 H

Significance: In 1986 Takai and co-workers developed a simple procedure for the stereoselective preparation of E-alkenyl halides from various aldehydes by using an excess of CrCl₂ together with a haloform. The selectivity was dependent on the corresponding haloform and decreased in the order Cl > Br > I.

Comment: The mild reaction conditions enable highly chemoselective transformations. Thus, the olefination of an aldehyde proceeds smoothly in the presence of ketone moieties. Given the unique chemo- and stereoselectivity, several modifications and improvements of this method have been published over the years.

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Key words

olefination stereoselectivity chromium catalysis

