If two halogen atoms are present in a given compound, reactions with reducing metals may take different paths depending on how close the carbon-halogen bonds are to each other. If they are separated by four or more carbons, as in the first example below, a bis-organometallic compound may be formed. However, if the halogens are bonded to adjacent (vicinal) carbons, an elimination takes place with formation of a double bond. Since vicinal-dihalides are usually made by adding a halogen to a double bond, this reaction is mainly useful for relating structures to each other. The last example, in which two halogens are bonded to the same carbon, referred to as geminal (twinned), gives an unusual reagent which may either react as a carbon nucleophile or, by elimination, as a carbene. Such reagents are often termed carbenoid.

The solution structure of the Simmons-Smith reagent is less well understood than that of the Grignard reagent, but the formula given here is as useful as any that have been proposed. Other alpha-halogenated organometallic reagents, such as CICH₂Li, BrCH₂Li, Cl₂CHLi and Cl₃CLi, have been prepared, but they are substantially less stable and must be maintained at very low temperature (ca. -100 °C) to avoid loss of LiX. The stability and usefulness of the Simmons-Smith reagent may be attributed in part to the higher covalency of the carbon-zinc bond together with solvation and internal coordination of the zinc. Hydrolysis (reaction with water) gives methyl iodide, confirming the basicity of the carbon; and reaction with alkenes gives cyclopropane derivatives, demonstrating the carbene-like nature of the reagent. The latter transformation is illustrated by the equation below.

Elimination reactions of the stereoisomeric 1,2-dibromo-1,2-diphenylethanes provide a nice summary of the principles discussed above. The following illustration shows first the meso-diastereomer and below it one enantiomer of the racemic-diastereomer. In each case two conformers are drawn within parentheses, and the anti-relationship of selected vicinal groups in each is colored green. The reaction proceeding to the left is a dehydrohalogenation induced by treatment with KOH in alcohol. Since this is a stereospecific elimination, each diastereomer gives a different stereoisomeric product. The reaction to the right is a dehalogenation (the reverse of halogen addition to an alkene), caused by treatment with iodide anion. Zinc dust effects the same reaction, but with a lower degree of stereospecificity. The mechanism of the iodide anion reaction is shown by red arrows in the top example. A similar mechanism explains the comparable elimination of the racemic isomer. In both reactions an anti-transition state is observed.

The two stereoisomers of 1-bromo-1,2-diphenylethene (shown on the left of the diagram) undergo a second dehydrobromination reaction on more vigorous treatment with base, as shown in the following equation. This elimination generates the same alkyne (carbon-carbon triple bond) from each of the bromo-alkenes. Interestingly, the (Z)-isomer (lower structure) eliminates more rapidly than the (E)-isomer (upper structure), again showing a preference for anti-orientation of eliminating groups.

\[
C₆H₅CH=CB₆H₅ + KOH \rightarrow C₆H₅C≡C₆H₅ + KBr + H₂O
\]

**Preparation of Alkynes by Dehydrohalogenation**

The last reaction shown above suggests that alkynes might be prepared from alkenes by a two stage procedure, consisting first of chlorine or bromine addition to the double bond, and secondly a base induced double dehydrohalogenation. For example, reaction of 1-butene with bromine would give 1,2-dibromobutane, and on treatment with base this vicinal dibromide would be expected to yield 1-bromo-1-butene followed by a second elimination to
1-butyne.

\[ \text{CH}_3\text{CH}_2\text{CH}≡\text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CBr} = \text{CH}_2\text{Br} + \text{base} \rightarrow \text{CH}_3\text{CH}_2\text{CH} = \text{CHBr} + \text{base} \rightarrow \text{CH}_3\text{CH}_2\text{C}≡\text{CH} \]

In practice this strategy works, but it requires care in the selection of the base and solvent. If KOH in alcohol is used, the first elimination is much faster than the second, so the bromoalkene may be isolated if desired. Under more extreme conditions the second elimination takes place, but isomerization of the triple bond also occurs, with the more stable isomer (2-butyne) being formed along with 1-butyne, even becoming the chief product. To facilitate the second elimination and avoid isomerization the very strong base sodium amide, NaNH$_2$, may be used. Since ammonia is a much weaker acid than water (by a factor of $10^{18}$), its conjugate base is proportionally stronger than hydroxide anion (the conjugate base of water), and the elimination of HBr from the bromoalkene may be conducted at relatively low temperature. Also, the acidity of the sp-hybridized C-H bond of the terminal alkyne traps the initially formed 1-butyne in the form of its sodium salt.

\[ \text{CH}_3\text{CH}_2\text{C}≡\text{CH} + \text{NaNH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{C}≡\text{C}(\text{(–)})\text{Na}(\text{+}) + \text{NH}_3 \]

An additional complication of this procedure is that the 1-bromo-1-butene product of the first elimination (see previous equations) is accompanied by its 2-bromo-1-butene isomer, CH$_3$CH$_2$CBr=CH$_2$, and elimination of HBr from this bromoalkene not only gives 1-butyne (base attack at C-1) but also 1,2-butadiene, CH$_3$CH=C=CH$_2$, by base attack at C-3. Dienes of this kind, in which the central carbon is sp-hybridized, are called allenes and are said to have cumulated double bonds. They are usually less stable than their alkyne isomers.

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**Contributors**