Alkenes from Epoxides by Reductive Elimination with Magnesium Bromide–Magnesium Amalgam

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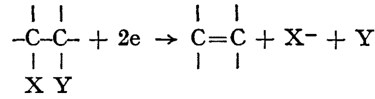
Summary Olefins may be obtained by treating epoxides in tetrahydrofuran solution with magnesium amalgam and magnesium bromide.

β-Substituted alkyl halides readily undergo a reductive elimination which can be represented as:

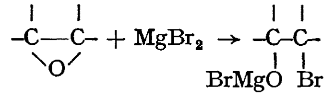


$$-\overset{|}{\underset{\underset{X}{|}}{C}}-\overset{|}{\underset{\underset{Y}{|}}{C}}- + 2e \rightarrow \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} + X^- + Y^-$$

X = halogen; Y = OH, OR, OCOR.

The best reducing agents for such systems are metals, *e.g.* sodium,[1] zinc,[2] and magnesium.[3]

On the other hand, epoxides react under appropriate conditions with metal halides, especially magnesium bromide in ether, to give, in many cases, the corresponding halohydrin salts:[4]



$$\underset{\diagdown O \diagup}{-\overset{|}{C}-\overset{|}{C}-} + MgBr_2 \rightarrow -\overset{|}{\underset{\underset{BrMgO}{|}}{C}}-\overset{|}{\underset{\underset{Br}{|}}{C}}-$$

We have observed that epoxides readily undergo reductive elimination on being stirred overnight with an equimolar amount of magnesium bromide in tetrahydrofuran or 1,2-dimethoxyethane in the presence of slightly more than 1 g.-atom of a dilute magnesium amalgam (0·5—3% Mg) at room temperature or, if necessary, at reflux, under nitrogen or argon.

Olefins are produced by this process from a variety of epoxides (Table). The yields are generally of the order of 30—40%. However, no effort has been made to increase the yields, and in many cases a considerable amount of starting material was recovered.

Table[a]

	% Yield[b]
1,2-Epoxy-1-phenylethane	32
1,2-Epoxy-1,1-diphenylethane	38
1,2-Epoxy-1-n-undecylethane	22
1,2-Epoxycyclohexane	50
3,3-Epoxymethylene-5α-cholestane[c]	80

[a] All products completely characterised.
[b] Yield of isolated, purified compounds.
[c] A mixture of isomers was employed.

The magnesium bromide etherate–magnesium amalgam mixture can easily be prepared by dissolving (under argon) in the appropriate quantity of mercury, 2·1 g.-atoms of magnesium, covering the resulting amalgam with solvent, and then treating, if necessary with cooling, with a mole of bromine.

The magnesium salt of a bromohydrin, resulting from the interaction between epoxide and magnesium bromide etherate, is most probably an intermediate in this reaction. This salt subsequently undergoes a magnesium-induced reductive elimination to the corresponding olefins.

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[1] H. House and R. Ro, *J. Amer. Chem. Soc.*, 1958, **80**, 182.

[2] L. Fieser and R. Ettore, *J. Amer. Chem. Soc.*, 1953, **75**, 1700; L. Crombie and S. Harper, *J. Chem. Soc.*, 1950, 1705, 1715; 1956, 136; S. Cristol and L. Rademacher, *J. Amer. Chem. Soc.*, 1959, **81**, 1600.

[3] R. Fuson, "Advanced Organic Chemistry," Wiley, New York, 1950, p. 144.

[4] *Cf.* for instance, E. T. McBee, C. E. Hathaway, and C. W. Roberts, *J. Amer. Chem. Soc.*, 1956, **78**, 3851; Houben-Weyl "Methoden der organischen Chemie," Thieme Verlag, Stuttgart, vol. 6/3, p. 437; C. A. Stewart and C. A. Vanderwerf, *J. Amer. Chem. Soc.*, 1954, **76**, 1259.