Grignard Coupling at High Temperatures

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The reaction $2RX + Mg \rightarrow MgX_2 + R\text{-}R$, in ether solution, occurs readily when R is an allylic group (*1*), to a small extent when R is alkyl (*1*), and apparently not at all when R is vinyl or a substituted vinyl group (*2*).

A method has been used which increases the yield of such reactions. The pure halide vapor is passed through a tube of magnesium turnings at temperatures over 250° C, in a helium atmosphere. Yields of 10% of octane are obtainable from one pass of *n*-butyl bromide at 330° C, at a rate of 3 ml/min through a tube of magnesium 18 mm in diam and 80 cm long. Unused halide may be recovered by distillation. The magnesium bromide (or chloride) forms a porous film on the magnesium and does not prevent it from reacting until it is substantially consumed.

When a vinyl halide (1-chloro-2-methyl-1-propene) was passed over magnesium in helium at 340° C, and the product distilled, a drift in physical properties at the end of the distillation indicated the presence of small amounts of octenes, but no identified product other than the starting material was isolated.

References

1. Boord, C. E. *et al.* *Ind. eng. Chem.*, 1949, **41**, 609.
2. Grignard, V. *Traité de chimie organique.* Paris: Masson & Cie.. 1935. Vol. 3, p. 354.

The Preparation of Formaldehyde-C^{14}[1]

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No satisfactory preparative method for formaldehyde-C^{14} has been reported. The production of this important intermediate has now been accomplished by an adaptation of the formaldehyde synthesis of Henry (*1*) and of Michael (*2*). Vacuum line technique was used.

Methyl-C^{14} acetate was prepared by reaction of methanol-C^{14} (*3*) with acetyl chloride. The monochlorination of methyl acetate to produce chloromethyl acetate, indicated by Henry to be favored by moderate temperatures, was performed in the present case by allowing a frozen equimolar mixture of chlorine and methyl-C^{14} acetate to warm to room temperature. The product, chloromethyl-C^{14} acetate, a methylenating agent (*5*), was readily hydrolyzed with excess water to produce a formalin solution of any desired concentration containing acetic and hydrochloric acids. Vacuum distillation of this solution gave para-formaldehyde as a residue and a more dilute formaldehyde solution as the distillate.

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The yield of formaldehyde solution from methanol was consistently about 60%, analyzed by precipitation of the dimedone derivative. The specific activity of formaldehyde-C^{14}-dimedone prepared by this procedure from methanol-C^{14} (12.00 μc/millimole) was 12.18 μc/millimole as determined by dry combustion and ion-current measurement by means of a vibrating reed electrometer (*4*).

Thirty millicuries of neutral formaldehyde solution of specific gravity 250 μc/millimole have been prepared by dilution of the hydrolysis solution with carrier formalin, neutralization, and distillation at atmospheric pressure.

Studies are in progress involving the chlorination of the methyl esters of other acids and use of formaldehyde-C^{14} and chloromethyl-C^{14} acetate as synthetic intermediates.

References

1. Henry, L. *Ber.*, 1873, **6**, 739.
2. Michael, A. *Amer. chem. J.*, 1879, **1**, 418.
3. Nystrom, R. F., Yanko, W. H., and Brown, W. G. *J Amer. chem. Soc.*, 1948, **70**, 441.
4. Palevsky, H., Swank, R. K., and Grenchik, R. *Rev. sci. Instr.*, 1947, **18**, 298.
5. Wood, F. *J. Soc. Chem. Ind.*, 1931, **50**, 411.

Determination of the Fate of Calcium in the Laying Hen by Means of Radiocalcium (Ca^{45})[1]

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Calcium metabolism in the laying hen can be studied with the aid of Ca^{45}. A direct approach to this problem is to replace the limestone powder in the mash by $CaCO_3$ containing Ca^{45} (*1*). In a typical experiment a hen ("A") was fed 1.71 g $CaCO_3$ with a Ca^{45} activity of approximately 2×10^6 cpm. The calcium in the eggs and droppings was separated in the usual way as CaC_2O_4 and its activity determined by means of a thin window Geiger counter. Corrections for decay and self-absorption were made. Total calcium was determined. The percentages of Ca^{45}, which are also the percentages of active $CaCO_3$, appearing in different parts of successive eggs are shown in Fig. 1.

The close similarity of this curve with that reported by Comar and Driggers (*2*), who administered 1 mg of radioactive calcium as a solution of the chloride to the lower esophagus of a fasted bird, is worthy of note. The recovery of calcium was at a maximum (29%) in the shell of the second egg and decreased very rapidly in the shells of later eggs. This is in agreement with the well-known fact that the shell is laid down in about 20 hr of oviposition. Fig. 2 shows the percent uptake of Ca^{45} in the shell, white, and yolk. The histogram for the yolk is

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