Highlights from the Literature

Some Items of Interest to Process R&D Chemists and Engineers, Selected by the Editor

We all have difficulty keeping up with the literature, and the increasing number of journals makes this an even more difficult task—of course *Organic Process Research & Development* has added to this too. Whilst I was in the library in central London a couple of weeks ago, I was browsing through some English translations of Russian journals. Much of the work in Russia is process orientated, but the methodologies used may be different from western technologies, so maybe there is something we can learn.

A recent review (Maretina, I. A. *Russ. J. Appl. Chem.* **1996**, *69*, 311) discusses the utilisation of diacetylene (1,3-butadiyne) in industrial organic synthesis. Whilst acetylene was originally used in the West as an alternative to petroleum feedstocks for basic organic synthesis—and there are still a number of processes which use acetylene as a raw material—in Russia there has been a resurgence of interest in acetylene chemistry in the last decade, partly as a result of development of methods of converting natural gas to acetylene. By-products from this process include higher acetylenes such as methylacetylene and diacetylene. The latter is highly reactive and, of course, tends to polymerise and decompose, often resulting in an explosion. As a result, processes in Russia involving flows of gases or ligands containing more than 10% diacetylene are banned.

The review indicates how processes to produce alkoxy and amino enynes can be operated safely, and some plant diagrams are given. These intermediates can be converted to carbonyl compounds, especially β-keto aldehydes in highly atom economical processes. This then leads to the synthesis of a wide range of heterocycles (pyridines, pyrazoles, etc.) and carbocycles.

In Russia, continuous processes for preparing Grignard reagents have been operated for many years. A recent description of a pilot process for making organosilanes from Grignard reagents (Klokov, B. A. *Russ. J. Appl. Chem.* **1995**, *68*, 100) reports yields of Grignard in the continuous process, starting with ethyl chloride, of 99%. The final silanes have low magnesium content.

A fuller description of the equipment used appears in an earlier review article by the same author (*Organomet. Chem. USSR* **1992**, *5*, 43). In this paper Klokov summarises 60 years of work on continuous Grignard processes in many companies/countries (74 references) with wide coverage of the patent literature. Klokov has developed processes for ethylmagnesium chloride and phenylmagnesium chloride from magnesium granules in a columnar apparatus with throughputs of from 7 to 40 kg/h of magnesium! The high throughput and economy, and the inherent safety associated with exothermic processes run in continuous mode, indicate that these processes may replace traditional batch processes for high-tonnage products.

Safety issues in the scale-up of batch Grignard processes are discussed by Dr. P. E. Rakita in a chapter in a recent book (*Handbook of Grignard Reagents*; Silverman, G. S., Rakita, P. E., Eds.; Marcel Dekker: New York, 1996; ISBN 0-8247-9545-8). Other chapters in this volume of interest to process chemists and engineers include "Magnesium Activation" and "Composition of Grignard Reagents in Solution", which discusses solvent effects. For those interested in Grignard technology, the volume contains over 700 pages of useful information.

Trevor Laird
Editor

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