Jean-François Normant

Organic bromo derivatives in organometallic reactions

Midway from the less reactive chlorocompounds and the more expensive iodo compounds, organic bromo derivatives have been extensively used in organometallic chemistry, so that this talk will not be a comprehensive survey but will focus on some particular points.

- From carbon-bromine to carbon-metal bond
  - via an M^o metal (Li, Mg, Cu, Zn, Cd) : improvements,
  - via an M^o metal under "Sayzev" (or "Barbier") conditions.
- R-Br compounds as electrophilic reagents towards organometallics influence of Ni^o, and Pd^oLn catalysis in the reaction of various bromo compounds with selected organometallics. Use of copper reagents in the coupling of RM + R' Br → RR'.
- Metal/bromine exchange
  with organolithium compounds - stereoselectivity - chiral reagents - lithio carbenoids.
  Gem dibromo derivatives as olefination reagents of carbonyl (carboxyl) compounds.
- Some examples on the influence of metallic bromides on the course of organometallic reactions will be discussed.

Pr Jean-François NORMANT - Université Pierre et Marie Curie - Paris (France).

Dans sa conférence sur : "Organic bromo derivatives in organometallic reactions".

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Bernard Langlois *

Reactivity of the carbon - bromine bond in perhalofluoromethyl and perhalofluoroethyl bromides

Bromine attached to a carbon atom bearing at least two fluorine substituents is not displaced by nucleophiles through a SN2 mechanism. Thus, perhalogenofluoroalkyl bromides can react with nucleophiles only through halophilic or monoelectronic reductive processes.

CF_2Br_2 and $BrCF_2CF_2Br$ are transformed essentially under halophilic conditions and lead, in a first step, to difluorocarbene and tetrafluoroethylene, respectively. Though few halophilic attacks are known upon CF_3Br, this compound is rather functionnalised under monoelectronic reductive conditions and lead primarily to the trifluoromethyl radical. Both types of reaction are observed with CF_2BrCl.

The substitution of bromine in CF_2Br_2, CF_2BrCl, CF_3Br and $BrCF_2Br$ will be illustrated by examples of synthetic and industrial interest.

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Almost all brominated organic flame retardants are used in combination with antimony trioxide as a true synergist. In combination with antimony trioxide, antimony halides are released in a step-wise manner, and these break down to form hydrogen halides which inhibit H• and •OH radicals as previously explained.

The processes for manufacturing brominated organic flame retardants vary from producer to producer. Many of these processes are known in the open literature through publications and patents. Brominations are carried out in a variety of organic solvents, and in some processes bromine itself is the solvent.

Great Lakes Chemical Corporation pioneered this unique process technology, which - as one would expect - is very cost effective. Most of the brominated organic flame retardants are high melting solids ground to fine particle size and very pure. There are some liquids, too, with a range of viscosities, boiling points and thermal stabilities.

There are many criteria considered in the selection of the best brominated organic flame retardant for a particular polymer system. The flame retardant may be simply an additive or a reactive component depending upon whether or not it becomes an integral part of the polymer system by chemical reaction. Key criteria considered in the selection process are : thermal stability, compatibility in the host polymer, dispersability, melting point, color, rheological properties, and light stability.

Brominated organic flame retardants are used in the complete range of plastic materials. Levels used vary from system to system. As little as 1 % by weight may be effective, but typically the level of flame retardant required to pass regulations ranges between 10 % and 25 % of the total finished compound by weight. When antimony trioxide is used as a synergist it is usually added at 25 % to 50 % of the weight of the bromine compound. Some particularly flammable compounds may require as much as 50 % by weight of flame retardants to be effective. Generally, the effectiveness of a brominated flame retardant is proportional to the percent bromine in the molecule.

Pr Thomas FIDELLE - Great Lakes Chem. Corp. - West Lafayette (USA).

Dans sa conférence sur : "Bromine in organic flame-retardants : Synthesis, uses, economical importance and new developments".

Most brominated organic flame retardants are aromatic in character ; however, there are a few aliphatic species - especially cycloaliphatic. The principal classes of brominated organic flame retardants are the brominated bisphenol-A's, the brominated diphenyl ethers and the brominated phthalic anhydrides. These compounds will be covered in detail in the final document. More will be said of specific applications plus trends and predictions for new products and regulatory activities.

Meir Englert

Bromine in the world

Bromine production worlwide has not increased substantially during the past fifteen years. Despite this, the number of bromine-based products has grown ten-fold during this period. The bromine industry is closely related to many facets of the chemical industry.

What trends will the bromine industry take in the near future ? This paper will try to outline some of the possible directions in response to this important question. Some of the characteristics of the world bromine market today are summarised.

In conclusion, the two dominant forces which will determine the future of the bromine industry are the growing reliance of the chemical industry upon specialities and society's increasing concern for environmental protection. For the industry to remains prosperous, these forces must cooperate for expansion. New uses for bromine compounds must be found - uses which will solve ecological problems rather than create them.

Dr Meir ENGLERT - Dead Sea Bromine - Beer Sheva (Israël).

Dans sa conférence sur : "Bromine in the world".

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