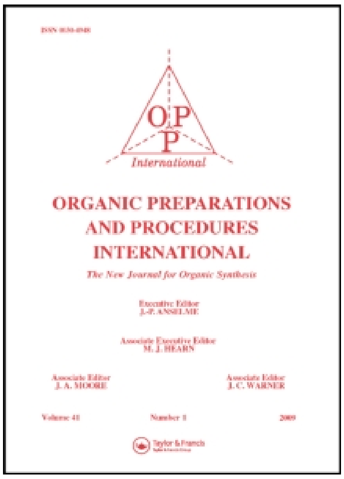

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REACTIVE ALUMINUM POWDERS FOR THE REDUCTION OF HALOARENES. APPLICATION OF THE “PLANNING OF EXPERIMENTS” METHOD FOR THE OPTIMISATION OF OBTAINING REACTIVE METAL POWDER

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REACTIVE ALUMINUM POWDERS FOR THE REDUCTION OF HALOARENES. APPLICATION OF THE "PLANNING OF EXPERIMENTS" METHOD FOR THE OPTIMISATION OF OBTAINING REACTIVE METAL POWDER

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The formation of Grignard reagents illustrates the richness of metallic surfaces activations.[1] Many discoveries span more than 90 years[2] and the Rieke's method involving the obtention of active Magnesium powder was discovered only in 1972.[3] The present paper applies Rieke's method of obtaining highly reactive powders of aluminum using the systematic approach of planning of experiments.[4] We have chosen the reaction between optimized aluminum powder and the haloaromatics for which Rieke reported the lowest yields of reaction. The importance of obtaining more reactive aluminum powders is emphasized in the reviews of Eisch, Yamamoto and Bardot.[5]

Chemical reactions may depend on diverse parameters such as temperature, pressure, amount of reagents. The traditional approach consists in studying each factor as if it were independent of the others, and usually does not take into account the interactions between these factors. The treatment of these factors within "the planning of experiments", method may lead to appreciable improvements in selectivity, purity, yields. The parameters that we studied experimentally between two poles (- and +) were a) temperature of dispersion with K (60° and 100° C); b) temperature of reduction with $AlCl_3$ (60° and 100°); c) time of reduction with $AlCl_3$ (1 h. and 3 h.); d) temperature of reaction with ArX; e) rate of stirring (ultra turrax (20.000 RMP) and ultra turrax + ultrasonic; f) additional effect of KI g) time of reaction with ArX (0.5 hr. and 2 hrs). The examples given in the Experimental Section correspond to the best selected parameters determined by such a methodology. Our experiments showed that although parameters b) and c) play the most important role, the others are far from negligible (the detailed set of experimental results may be obtained from the authors). Remarkably, the addition of potassium iodide to the mixture prior to reduction, had little effect for aluminum activation. However, Rieke found that this factor was of importance for obtaining active magnesium powders.[6,7] The determination of the best experimental conditions (see Experimental), led to quantitative reduction of both chlorobenzene and p-fluorotoluene. This result is significant because Rieke showed that p-fluorotoluene is the most unreactive of the haloarenes in the reaction towards activated Mg.[3],[7] Most of the reported catalyzed reductions of haloarenes apply to iodides, bromides and sometimes chlorides but not to fluorides.[8,9]

The activation of aluminum by Rieke's method[10] was a significant step compared with previous methods of activation.[11] The present work shows that even the worst yields may still be improved by planning of experiments methodically. This is noteworthy because activation by reduction of metal compounds is involved in an increasing number of different processes.[12] The large number of variable experimental parameters could lead one to wonder if good and reproducible yields are actually obtainable; they are. For aluminum itself, this approach suggests that potassium with an increased reducing power (Na or K naphthalenide[13],[14]) could allow the obtention of even more active powders for reactions with least reactive haloarenes and/or metal halides.

EXPERIMENTAL SECTION

Reaction of Chlorobenzene with Activated Aluminum Powder. Typical Procedure.- Freshly cut potassium (60 mmole, 2.34 g) was placed in a 200 ml three-necked flask with a sidearm equipped with a septum cap in a Dry Box. Then freshly distilled xylene (75 ml) was added and the mixture was heated at 100° (above the melting point of the alkali metal), to give a dispersion of the alkali metal (potassium) in xylene (potassium sand). Then, 22 mmoles (2.95 g) of anhydrous $AlCl_3$ (puriss > 99%, less than 0.008% of Fe) were added under nitrogen to the cooled (50°) potassium sand suspension and mixed using either a homogeniser ultra turrax (up to 20,000 RPM) or ultra turrax (U.T.)-ultrasonic combination. The finely divided black aluminum metal was generated within 1 hr. Then chlorobenzene (10 mmoles) was added over a period of 30 min. and the mixture stirred at 100°. The color of the mixture changed from black to brown. Aliquots were quenched in 10% HCl solution and an internal chromatographic standard was added. The organic layer was dried over $CaSO_4$ and analyzed by vpc. The yield was determined by measuring the appearance of benzene and disappearance of chlorobenzene. The yield of benzene obtained by this method showed the quantitative reduction of chlorobenzene.

Reaction of p-Fluorotoluene with Activated Aluminum Powder. Typical Procedure.- The same experimental process (identical concentrations, temperatures, time of addition, stirring, absence of KI) provides a quantitative yield of toluene from p-fluorotoluene.

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A CONVENIENT PREPARATION OF 9-DIMETHYLAMINO-10-CARBOMETHOXYANTHRACENE

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The novel title compound 4 was required in connection with a study of extended conjugation in triarylmethane dyes;[1] the immediate precursor, 9-