

Preparative catalytic chlorination of adamantane, cyclohexane, and hexane in the system tetrachloromethane-MX₂(PPh₃)₂ (MX₂ = PdBr₂, PtCl₂)-acetonitrile-potassium carbonate

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Abstract

Heating of saturated hydrocarbons RH (cyclohexane, adamantane, and hexane) with tetrachloromethane in the presence of acetonitrile, potassium carbonate, and catalytic amounts of dihalide triphenylphosphine complexes of palladium(II) or platinum(II), MX₂(PPh₃)₂ (MX₂ = PdBr₂, PtCl₂), for 6-8 h at 120°C yields monochlorinated derivatives of the respective hydrocarbons in 30-55% yield. Benzene, toluene, ethylbenzene, and tetramethylsilane show low reactivity under the conditions adopted for the reaction. Relative reactivity of various bond types C-H of alkanes is in agreement with the well known sequence: tertiary > secondary > primary. A scheme is proposed assuming trichloromethyl radicals as active species, and the catalyst function consists in activating C-Cl bond of the tetrachloromethane. © 1998 MAHK Hayka/Interperiodica Publishing.
