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Journal of Organometallic Chemistry 601 (2000) 341–342

Journal of Organo metallic Chemistry

Note

On the in situ trimethylsilylation of zinc acetylides

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Received 15 November 1999; received in revised form 31 January 2000

Abstract

Reinvestigation of the recently published formation of silylated alkynes by reaction of 1-alkynes with zinc and trimethylchlorosilane in acetonitrile showed that appreciable amounts of 1-alkenes are formed as side products. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Trimethylacetylenes; Silylation; Reduction; Alkenes; Zinc powder

The versatility of 1-alkynes RC≡CH as starting reagents in organic syntheses has led to the development of efficient functionalization methods. The first step mostly involves metallation with a Grignard reagent or a strongly basic reagent, e.g. *n*-butyllithium [1,2]. Recently, Japanese chemists [3,4] reported the formation of silylated alkynes in good to excellent yields by heating a mixture of the 1-alkyne, excess of trialkylchlorosilane and zinc powder in acetonitrile. They claim superiority of their method to the existing ones. Being interested in efficient synthetic procedures (compare Ref. [2]), we decided to repeat the published procedure on a preparative (0.10 M) scale taking the silylation of PhC≡CH as a model. This reaction was carried out under atmospheric pressure.

A magnetically stirred mixture of 30 g of zinc powder (Merck, analar grade, particle size < 60 μm), 21.6 g (0.20 mol) of trimethylchlorosilane (distilled from 5% (w/w) of *N*,*N*-diethylaniline) and 60 ml of acetonitrile (analar grade, distilled from calcium hydride) was heated under reflux under an atmosphere of nitrogen. After about 10 h no further increase of the temperature in the boiling mixture (moderate, constant reflux) was observed (~74→80°C) while GLC had shown complete consumption of PhC≡CH. The excess of Me_3SiCl was distilled off as completely as possible from the stirred mixture. When CH_3CN began to pass over, the mixture was cooled to 20°C and the clear supernatant liquid was decanted from the excess of zinc and poured into 200 ml of water. The remaining slurry of zinc and CH_3CN was washed repeatedly with pentane (total volume ~150 ml). The combined organic solutions were washed four times with water in order to remove the CH_3CN. After drying over $MgSO_4$, the pentane was distilled off at atmospheric pressure. Careful vacuum distillation (30 cm Vigreux column) gave a volatile first fraction (4.0 g, consisting of ~30% of $Me_3SiOSiMe_3$ and 70% of styrene), and a main fraction of Ph≡CC–$SiMe_3$ (b.p. 90 KC/15 mmHg) in 63% yield. There was no residue after distillation. The products were analysed with ^{1}H-NMR and GLC (identity with authentic samples).

The reaction time could be shortened to about 5 h by using activated zinc powder: a mixture of 35 g Zn, 50 ml of dry THF and 5 g of 1,2-dibromoethane was heated under reflux (~30 min) until evolution of

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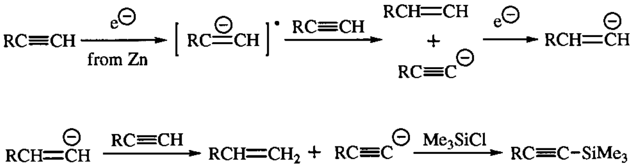
PII: S0022-328X(00)00103-0

ethene had stopped. After cooling, the THF was decanted and the remaining slurry rinsed several times with CH_3CN in order to remove the THF.

Reactions with $HC{\equiv}C(CH_2)_9OH$ and $HC{\equiv}C{-}n{-}C_{10}H_{21}$ were also carried out with zinc activated by treatment with 1,2-dibromoethane. The rates of conversion of these acetylenes were much lower than that of $PhC{\equiv}CH$. After 5 h refluxing work-up was carried out and the product mixture analysed with GLC and ^{1}H-NMR spectroscopy, 45% (rel.) of undecynol and 22% of dodecyne still being present. In addition the reduced alkynes $H_2C{=}CH(CH_2)_9OH$ (11%) and $H_2C{=}CH{-}C_{10}H_{21}$ (22%) had formed, together with the TMS-derivatives $Me_3SiC{\equiv}C(CH_2)_9OH$ (44%) and $Me_3SiC{\equiv}CC_{10}H_{21}$ (61%). Also, Sugita et al. [3] found reduction to be a significant side reaction in several cases when a Zn/Cu couple was used, whereas with the same kind of activated zinc they obtained $PhC{\equiv}CSiMe_3$ in an excellent yield and no styrene was formed. The formation of olefinic compounds may be explained by an electron transfer–deprotonation mechanism, similar to the sequence involved in the preparation of alkali acetylides from alkali metals and acetylene in liquid ammonia [5].



According to this mechanism the maximally attainable yield of silylated acetylenes is 66%, which compares with the yield obtained by us from the reaction with $PhC{\equiv}CH$.

It seems to us that a more thorough investigation is necessary to reveal the cause of the discrepancies observed.

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