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ORGANIC SONOCHEMISTRY. ULTRASOUND PROMOTED COUPLING OF CHLOROSILANES IN THE PRESENCE OF LITHIUM WIRE

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Abstract. Triorganometal chlorides, R_3MCl (R = alkyl, aryl; M = Si, Sn) are readily coupled to form bimetallics in 42-95% yields using Li wire and ultrasound. Dihalosilanes give good yields of cyclic polysilanes.

Sonic waves have been used sparingly in synthesis, although the number of applications is growing.[1-6] The recent communications describing the coupling of organic bromides with ketones[5] and the Wurtz-type coupling of organic halides (aryl, benzyl, benzoyl and alkyl)[6] are the most successful examples of this technique and indicate considerable potential for its use.

In this paper we report that ultrasound also facilitates the coupling of chlorosilanes to give disilanes in good yields. Our results are summarized in the Table.

$$R_3SiCl \xrightarrow[Li]{)))))} R_3Si\text{-}SiR_3$$

Table. Ultrasound Induced Reaction of Chlorosilanes with Lithium

Chlorosilane	Disilane	Solvent	Time (h)	Isolated Yield(%)
Ph_3SiCl	$Ph_3SiSiPh_3$	C_6H_6:THF(2.5:1)	10	73
Ph_2HSiCl	$Ph_2HSiSiHPh_2$	THF	10	68
Et_3SiCl	$Et_3SiSiEt_3$	THF	60 (2)[a]	15 (58)[a]
Me_3SiCl	$Me_3SiSiMe_3$	THF	24 (2)[a]	9 (42)[a]

[a] Lithium dispersion (30% in mineral oil) and 0.6 g anthracene used

In a typical experiment, 0.01 mol of triphenylchlorosilane was added to 3-5 ml of dry THF and 0.02 mol of lithium wire (1/4" x 1/8") in a 25 ml flask partly submerged in a common ultrasound laboratory cleaner (117 v, 150 w, 50/60 Hz). The major product was isolated by crystallization and the yield was not optimized. In most runs by-products such as Ph_3SiH and $Ph_3SiOSiPh_3$

totalled no more than 5% and never exceeded 10%. In the absence of ultrasound no reaction was observed. Typically, the coupling of chlorosilanes requires high speed stirring and some heating.

In our studies of the coupling of organic halides by lithium in the presence of ultrasonic waves we obtained isolated yields as high as 73% of dimer. n-Butyl chloride, for example, gave a 72% yield of octane.[6] We were disappointed then, when Me_3SiCl and Et_3SiCl gave low yields under the same conditions. The reaction improved significantly however, using lithium dispersion and a small amount of anthracene. In these cases the reaction mixtures were dark blue in contrast to the deep red color of the Ph_3SiCl and Ph_2HSiCl examples. The hexaalkyldisilanes were isolated by distillation.

Sonic acceleration of coupling is not limited to silicon and carbon.[6] Trialkyltin halides (R = Me, n-Bu) gave good yields of hexamethyldistannane (60%) and hexa-n-butyldistannane (94%) with lithium wire in THF. No anthracene was required.

We have also initiated a study of dichlorosilanes and found that oligomerization to cyclopolysilanes is the principal reaction. When R = Me or Ph, for example, good yields (70-95%) of dodecamethylcyclohexasilane and octaphenylcyclotetrasilane, respectively, were obtained. Both products were contaminated with cyclopentasilanes, however. Silylene intermediates do not appear to be involved. When Me_2SiCl_2, Et_3SiH, Li and anthracene were sonicated, $Et_3SiSiMe_2H$, the silylene insertion product, was not observed.

Work is now in progress to extend this coupling reaction to the synthesis of novel disilanes as well as to other bimetallics.

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