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Ultrasound in organometallic chemistry. The effects of temperature, metal purity and power source on the ultrasound-promoted reaction between trimethylchlorosilane and lithium

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Abstract

The temperature, lithium purity, and the source of ultrasound (bath or probe) all have significant effect on the ultrasound-promoted reaction between Me_3SiCl and Li to give $Me_3SiSiMe_3$.

1. Introduction

The use of ultrasound in organic and organometallic chemistry has become increasingly common in recent years and several books on sonochemistry have appeared recently [1a–c]. Despite this rapid growth of interest few systematic studies have been carried out on synthetically useful reactions in which the effects of temperature, intensity of ultrasound, *etc.* have been examined. This has led to some problems of irreproducibility (see for example refs. 2 and 3 in which different products are reported for the ultrasound promoted reaction between $mesityl_2SiCl_2$ and Li) and some confusion about how best to carry out a sonochemical reaction.

Ten years ago Boudjouk and his group demonstrated that couplings of alkyl and aryl halides and of chlorosilanes and halostannanes by use of lithium metal were accelerated by irradiation by ultrasound [4]. The yields of $Me_3SiSiMe_3$ and $Et_3SiSiEt_3$ from Me_3SiCl and Et_3SiCl respectively, were only 9 and 15% after 24 and 60 h sonication, respectively, although these yields were increased to 42 and 58% when lithium dispersion with added anthracene was used instead of lithium wire. We have studied in detail the ultrasound-promoted reaction between Me_3SiCl and Li in tetrahydrofuran (THF) and have used it as an example for the study of some of the factors that are important in organometallic sonochemistry. We have found the reaction to be highly sensitive to the quality of the lithium, the temperature at which the reaction is carried out, and the intensity of the ultrasound used.

2. Experimental details

2.1. General

The two sources of lithium used were May and Baker (lumps containing 2% sodium) and Aldrich lithium rod (99.9%) supplied dry under argon. Before use the high sodium content lithium was rinsed with hexane to remove the paraffin oil in which it was supplied. In both cases the lithium was prepared for use by beating it into a foil approximately 1 mm thick and then cutting it with scissors directly into the reaction vessel. Tetrahydrofuran was distilled from sodium benzophenone ketal immediately prior to use and Me_3SiCl (Lancaster Synthesis) was used as supplied. All reactions were carried out under dry nitrogen.

The ultrasonic bath used was a Kerry Pulsatron 125 model operating at a frequency of $38 \pm 10\%$ kHz. The probe, a Sonics and Materials VC300, operated at a frequency of 20 kHz and at power level 8. Owing to the potentially dangerous sound levels generated by the probe it was housed, together with the reaction vessel, in a soundproof cabinet. For any adjustments to the reaction vessel while a reaction was taking place to be

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carried out the experimenter wore ear protectors. Reactions in the ultrasonic bath were carried out in a 100 ml round-bottomed flask and the reactions using the probe were carried out in either a Suslick cell (adapted to have ground glass joints) or a rosette cell. Diagrams of the general arrangement of the reaction vessels in each case are as given in ref. 5. The volume of solvent used in the Suslick cell was 15 cm^3 and that in the rosette cell 50 cm^3.

The progress of the reaction in each case was monitored by ^1H NMR spectroscopy. At various times irradiation was stopped, a sample withdrawn and its NMR spectrum recorded immediately. The integrals of the signals due to Me_3SiCl and $Me_3SiSiMe_3$ were compared (with allowance for the different numbers of protons present in each) to reveal the extent of reaction. The sample was then returned to the reaction vessel and the sonication continued.

2.2. Example procedure

Trimethylchlorosilane (0.05 mol) was added to a mixture of dry THF (25 cm^3) and lithium (0.1 mol) in a 100 ml round-bottomed flask partly submerged in the ultrasonic bath. The bath was then turned on and the reaction was monitored as described above. For fixed temperature experiments crushed ice, which was prevented from coming between the base of the bath and the bottom of the flask by a plastic mesh, was added to the water in the bath. The temperature was monitored by periodically turning off the bath for a short time and inserting a thermometer into the reaction flask. For experiments in which the temperature varied the bath temperature was allowed to rise as a result of the natural warming that occurred because of the heating effect of the ultrasound on the bath water as the reaction proceeded.

Reactions carried out in the Suslick cell were on a third of the scale used for the bath experiments, although a 20% excess of lithium was used because occasionally small pieces of lithium became trapped by the metal collar holding the cell and were, therefore, lost from the reaction. The cell was immersed in an ice-water or CCl_4-dry ice slush bath to maintain an even temperature in all experiments, and again a thermometer was periodically inserted into the reaction vessel to monitor the temperature.

3. Results and discussion

When the reaction between the lithium (99.9% pure) and Me_3SiCl was attempted without ultrasonication and agitation was by magnetic stirrer bar, no reaction was observed, although less than about 5% of product would probably have escaped measurement, either over a period of 23 h at room temperature or over 16 h at reflux. In contrast, the stirred reaction using the lithium containing sodium proceeded to 50% in 23 h at room temperature and 97% in 9 h under reflux. A 97% yield of $Me_3SiSiMe_3$ from the reaction between lithium dispersion and Me_3SiCl in refluxing THF for 8 h was previously reported [6]. It is well known that sodium is an effective metal for the polymerization of chlorosilanes, and in this case it is likely that the reaction is initiated by the sodium and the relatively slow reaction with lithium occurs as the reaction with sodium keeps the surface of the bulk metal clean. With no sodium present the stirring action used is not vigorous enough to break down unreactive surface layers on the metal thus exposing fresh metal.

The quality of the lithium used had less effect on the reaction carried out at 25–28°C (with ice-water cooling the cell) when subject to high power ultrasound provided by the probe system. Table 1 shows that both reactions were essentially complete within 4 h (20% excess lithium was present in the reactions; see Experimental section) although for reasons that are unclear that involving the low sodium lithium was slightly faster. The effect of the ultrasound is thus to give a rapid reaction where none was observed in the stirred reaction with the pure lithium and the reaction rate was greatly increased (having a half-life approximately 20 times shorter) in the second case. In a single reaction carried out at between 10 and 15°C (using a CCl_4-dry ice slush bath as coolant) an essentially quantitative yield of the disilane was obtained after 85 min when a 5% excess of the lithium containing 2% sodium was used.

When the bath was used as the ultrasound source the effects of temperature could also be seen. Tables 2 and 3 show how the reaction proceeded when the lithium and the temperature were varied. At constant temperature (*ca.* 7°C) with either type of lithium the reactions are, as expected, faster than the stirred reactions but slower than those carried out with the probe. As in the stirred reaction, the high sodium content

TABLE 1. Yields of $Me_3SiSiMe_3$ from the reaction between Me_3SiCl and Li accelerated using the ultrasonic probe

Li/2% Na [a] 25–28°C		Li/2% Na 10–15°C		Li/0.02% Na [b] 25–28°C	
Time (h)	Yield (%)	Time (min)	Yield (%)	Time (h)	Yield (%)
1	26	20	26	1	27
2	50	45	52	2	60
3	66	70	71	3	96
4	100	90	100	3.5	100

[a] Average results of three reactions. [b] Average results of two reactions.

TABLE 2. Yields of $Me_3SiSiMe_3$ from the reaction between Me_3SiCl and Li at constant temperature (7°C) accelerated by the ultrasonic bath

Li/2% Na		Li/0.02% Na [a]	
Time (h)	Yield (%)	Time (h)	Yield (%)
1	13	1	5.5
2	28.5	2	8
3	48	3	17
4	61	4	24
5	72	5	32
6	73	6	38
7	76	7.5	52
		9	57
		10	58.5

[a] Average results from two reactions.

lithium gives a faster reaction. When the temperature was allowed to increase as the bath warmed up owing to the heating effect of the ultrasound passing through the bath the reactions started rapidly but slowed as the temperature increased (the opposite effect to that expected for a simple stirred reaction) and little reaction was observed above 45–50 °C. No excess of lithium was used in these reactions.

The rate increases found in the reactions subjected to ultrasound can be seen as due to the effects of cavitation, which have been discussed at length by others [1a–c]. The important effects in these reactions seem to be the cleaning of the metal surface (both from unreactive metal oxide or nitride at the start of the reactions and from lithium chloride formed as the reactions progress) so that a reactive surface is always in contact with the chlorosilane, a reduction in particle size, and the temperature. The lithium pieces at the start of the reactions were roughly triangular and approximately 1 mm thick and 3 to 5 mm on each side, and after a short time the effect of the ultrasound was to reduce them to a powder, thus increasing the surface area available for reaction. The formation of a dispersion of finely divided lithium in THF is in contrast to the suggestion by Einhorn *et al.* that lithium dispersions are not formed in this solvent [7]. It is not clear why formation of dispersion occurred in this work and not previously. The decrease in rate on increasing the temperature when the bath was used is due to the decrease in cavitation activity as the boiling point of the solvent is approached and the vapour pressure increases. Optimum temperatures for cavitation in various solvents have been tabulated [8] and the effect of solvent vapour pressure on cavitation has been described before [1a–c]. It should be noted that the temperature of a reaction solution may rise rapidly, particularly when the ultrasonic probe is used, owing to the ultrasonic power input. This means that the reactions must be cooled adequately and the temperature recorded *inside* the reaction vessel as there may be a considerable difference in temperature inside and outside the vessel.

TABLE 3. Yields of $Me_3SiSiMe_3$ from the reaction between Me_3SiCl and Li allowing the reaction temperature to increase during the reaction in the ultrasonic bath

Li/2% Na			Li/0.02% Na [a]		
Temp. (°C)	Time (h)	Yield (%)	Temp. (°C)	Time (h)	Yield (%)
11	0	0	11	0	0
26	1	28	26	1	9
36	2	35	36	2	18
40	3	38	40	3	24
44	4	40	44	4	28
46	5	42	46	5	33
48	6	44	48	6	35

[a] Average results from two reactions.

The rates found in this work for the reactions carried out in the bath are roughly the same as those of Boudjouk [4] when using lithium dispersion and added anthracene, and somewhat greater than those obtained by Boudjouk with lithium wire (99.99% Li, [9]). This suggests that the particle size reduction found in our work is an important factor, although the temperature at which the reactions were carried out was not reported in ref. 4. The temperature can, from this work, be seen to be important, particularly so in lengthy reactions (e.g. 24 h for a reaction giving only 9% of the product in ref. 4) as the bath can easily warm to temperatures at which cavitation is poor in THF.

These reactions demonstrate that for sonochemical reactions of this type the increased power available from an ultrasound horn increases the reaction rate, as expected. The temperature at which the reaction is carried out is also important, and should be chosen such that cavitation is maximized for the particular solvent used. Finally, it should be noted that the efficiency of different ultrasonic baths varies greatly, and also that within a particular bath the activity varies and so the reaction vessel should be placed in a position of maximum agitation.

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References

1 (a) S.V. Ley and C.M.R. Low, *Ultrasound in Synthesis,* Springer-Verlag, Berlin, 1989; (b) K.S. Suslick (ed.), *Ultrasound, Its Chemical, Physical, and Biological Effects,* VCH, Weinheim, 1988; (c)

T. J. Mason and J. P. Lorimer, *Sonochemistry, Theory, Applications and Uses of Ultrasound in Chemistry,* Ellis Horwood, Chichester, 1988.
2 P. Boudjouk, B. Han and K. R. Anderson, *J. Am. Chem. Soc.,* 104 (1982) 4992.
3 S. Masamune, S. Murakami and H. Tobita, *Organometallics*, 5 (1983) 1464
4 P. Boudjouk and B. H. Han, *Tetrahedron Lett., 22* (1981) 3813.
5 S. V. Ley and C. M. R. Low, *Ultrasound in Synthesis*, Springer-Verlag, Berlin, 1989, pp. 18, 22 and 23.
6 D. E. Seitz and L. Ferreira, *Synth. Commun., 9* (1979) 451.
7 C. Einhorn, J. Einhorn and J.-L. Luche, *Synthesis* (1989) 787.
8 S. V. Ley and C. M. R. Low, *Ultrasound in Synthesis*, Springer-Verlag, Berlin, 1989, p. 7.
9 P. Boudjouk, personal communication.