ELSEVIER

Journal of Organometallic Chemistry 510 (1996) 167–172

Journal of Organometallic Chemistry

Rate increases in the fluorination of bulky chlorosilanes caused by ultrasound or by water

Paul D. Lickiss [1,*], Ronan Lucas [2]

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

Received 10 July 1995

Abstract

The conversion of bulky chlorosilanes to fluorosilanes under anhydrous conditions with hexafluorosilicate salts is accelerated by ultrasound. The fluorination of sterically hindered chlorosilanes such as ^{t}BuPh$_2$SiCl, in the absence of ultrasound, is greatly accelerated by the addition of water to the reaction mixture.

Keywords: Silicon; Fluorination; Ultrasonic activation

1. Introduction

Fluorosilanes can be used for a variety of purposes, e.g. in the preparation of pentacoordinate silicon anions and of highly hindered organosilanes [1–3]. It has also been found that alkylation reactions of potassium 18-crown-6 salts of the organofluorosilicates $[R_2SiF_3]^-$ and $[R_3SiF_2]^-$ are more rapid than direct reactions of the corresponding four-coordinated silanes R_3SiF [4]. There are many methods available for the conversion of chlorosilanes into fluorosilanes that give high yields but most suffer some disadvantages [5] such as the cost or toxicity of the reagents or the requirement of harsh reaction conditions. In seeking reagents which would convert chlorosilanes into fluorosilanes which would be safe and easy to handle, as well as inexpensive, Damrauer et al. [6] studied the reactivity of hexafluorosilicates towards chlorosilanes. They found that both $(NH_4)_2SiF_6$ and Na_2SiF_6 could give complete conversion, the best results being obtained with $(NH_4)_2SiF_6$ in 1,2-dimethoxyethane (DME): However, when bulky silanes such as ^{t}Bu$_2$SiCl$_2$ were used. 2 weeks were needed to achieve a good yield.

$$R_2SiCl_2 + (NH_4)_2SiF_6 \xrightarrow{\text{DME,85°C}} R_2SiF_2 + 2NH_4Cl + SiF_4 \qquad (1)$$

R = Ph, Mes or ^{t}Bu

Ultrasound is commonly used to increase reaction rates and yields and also to allow the use of reduced temperatures for heterogeneous reactions (for reviews of its use in synthetic chemistry see [7]). The use of ultrasound thus seemed appropriate for the fluorination of chlorosilanes, as the low solubility of the hexafluorosilicate salts in dimethoxyethane could be a key factor in the long reaction times needed.

2. Results and discussion

The first set of reactions was carried out in order to investigate the influence of ultrasound intensity (probe or cleaning bath), solvent (DME or tetrahydrofuran (THF)), salt [$(NH_4)_2SiF_6$ or Na_2SiF_6], and salt stoichiometry (1/1 or 1/2 equivalent), on the fluorination of Ph_2SiCl_2. The results are summarized in Table 1. Before reactions were carried out in the presence of ultrasound, two reactions from the literature were repro-

---

[*] Corresponding author.

[1] Present address: Department of Chemistry, Imperial College of Science Technology and Medicine, South Kensington, London SW7 2AY, UK.

[2] Present address: CEA, BP 12, 91680 Bruyères-Le-Chatel, France.

SSDI 0022-328X(95)05868-0

duced, one with Ph_2SiCl_2 and one with Mes_2SiCl_2, (Mes = mesityl) using refluxing DME (boiling point (b.p.), 85°C; reagent grade; water content unknown), and dry $(NH_4)_2SiF_6$. The course of the reaction was monitored by gas–liquid chromatography (GLC) and ^{19}F NMR spectroscopy and the results were similar to those previously reported (Table 1, entries 1 and 9) [6]. The conversion of Ph_2SiCl_2 into Ph_2SiF_2 using the ultrasonic cleaning bath at room temperature and $(NH_4)_2SiF_6$ was slower, taking 3 h (Table 1, entry 2) and giving a by product thought to be $Ph_2SiF(OH)$. This presumably arises from partial hydrolysis of Ph_2SiCl_2 by adventitious water in the system to give $Ph_2SiCl(OH)$ as an intermediate. The Ph_2SiCl_2 was all consumed within 1.5 h yielding 81.9% Ph_2SiF_2 as well as 18.1% $Ph_2SiF(OH)$, and a further 1.5 h were required to fluorinate most of the $Ph_2SiF(OH)$. This showed that an Si–OH group could be converted to an Si–F group by $(NH_4)_2SiF_6$. The reaction using the ultrasonic probe (Table 1, entry 3) showed a considerable rate increase as no starting material was visible on the GLC trace after 8 min, and a further 12 min were needed to convert the hydroxy by product, giving 98% of the difluorosilane in a total of 20 min. The use of a 1/1 stoichiometric amount of $(NH_4)_2SiF_6$ in DME with the probe (Table I, entry 4) gave the same yield as that with a 100% excess but in double the time. The results with the probe demonstrate that ultrasound allows the use of a lower reaction temperature and increases the rate of this heterogeneous reaction. This is probably due to acoustic streaming, resulting in a better mixing of the reagents.

The fluorination of $Ph_2Si(OH)_2$ using the probe was attempted with a higher concentration of silicon compound and of hexafluorosilicate salt than in the previous experiments (0.3 M instead of 0.1 M). The conversion was slow but, after 3 h, two signals in the ^{19}F NMR spectrum and on the GLC trace, with the same chemical shifts and retention times as the products obtained from the fluorination of Ph_2SiCl_2 were seen, suggesting that slow direct fluorination of silanols is possible when ammonium hexafluorosilicate is used. It has been shown that Si–Si, Si–H and Si–O–Si bonds are not affected by $(NH_4)_2SiF_6$ [6], and we found that an attempted fluorination of the cyclotetrasiloxane $(Ph_2SiO)_4$ with sonication by the probe for 4 h gave back the starting material quantitatively.

Changing the salt to Na_2SiF_6 (Table 1, entry 5) resulted in a lower rate of reaction, and the formation of $Ph_2SiF(OH)$ was much more important: after 3 h, 68% Ph_2SiF_2 plus 32% $Ph_2SiF(OH)$ were identified on the GLC trace. When THF (Table 1, entries 6 and 7) was used instead of DME, with the cleaning bath or with the probe, the rates were lower. With the bath the reaction

Table 1
Fluorination of chlorosilanes using a reagent grade solvent

Entry	Starting material	Method [a]	Solvent	Time	Yield [b] (%)	Product
1	Ph_2SiCl_2	Reflux	DME	45 min	100 (65)	Ph_2SiF_2
2	Ph_2SiCl_2	Cleaning bath	DME	3 h	94 (72)	Ph_2SiF_2
					6	$Ph_2SiF(OH)$
3	Ph_2SiCl_2	Probe	DME	20 min	98 (82)	Ph_2SiF_2
					2	$Ph_2SiF(OH)$
4	Ph_2SiCl_2	Probe [c]	DME	40 min	98	Ph_2SiF_2
					2	$Ph_2SiF(OH)$
5	Ph_2SiCl_2	Probe [d]	DME	3 h	68	Ph_2SiF_2
					32	$Ph_2SiF(OH)$
6	Ph_2SiCl_2	Cleaning bath	THF	5 h	91	Ph_2SiF_2
					9	$Ph_2SiF(OH)$
7	Ph_2SiCl_2	Probe	THF	1.75 h	98	Ph_2SiF_2
					2	$Ph_2SiF(OH)$
8	Ph_3SiCl	Reflux [e]	DME	19 h	100	Ph_3SiF
		Probe	DME	1.25 h	99 (78.9)	Ph_3SiF
					1	Ph_2SiF_2
9	Mes_2SiCl_2	Reflux	DME	18 h	100 (81)	Mes_2SiF_2
		Probe	DME	4 h	52	Mes_2SiF_2
					7	$Mes_2SiF(OH)$
10	$^tBu_2SiCl_2$	Reflux [e]	DME	2 weeks	100	$^tBu_2SiF_2$
		Probe	DME	3 h	< 5	$^tBu_2SiF_2$
11	$^tBuPh_2SiCl$	Reflux [e]	DME	120 h	70	$^tBuPh_2SiF$
		Probe	DME	3 h	0	—

[a] Reaction conditions if not specified: cleaning bath, 25°C; 100% $(NH_4)_2SiF_6$ excess.
[b] GLC yield followed by isolated yield in parentheses.
[c] 1/1 equivalent $(NH_4)_2SiF_6$.
[d] 100% Na_2SiF_6 excess.
[e] Data taken from [6].

Table 2
Fluorination of chlorosilanes with $(NH_4)_2SiF_6$ in anhydrous dimethoxyethane

Entry	Starting material	Method [a]	time	GLC yield (%)	Product
1	Ph_2SiCl_2	Cleaning bath	80 min	98	Ph_2SiF_2
2	Ph_2SiCl_2	Probe	8 min	100	Ph_2SiF_2
3	Ph_3SiCl	Probe	2.75 h	92 (71)	Ph_3SiF
				3	Ph_2SiF_2
4	Mes_2SiCl_2	Probe	3 h	0	—

[a] Cleaning bath, 25°C; probe, 25°C.

was carried out at 5°C to try to get the best ultrasonic effects for THF (the optimum temperature for cavitation in THF has been reported to be 0°C [8]) as the solvent, but the lowering of the temperature also reduces the solubility of the fluorinating agent. When the probe and THF were used, the reaction temperature was the same as that in DME (25°C) but 1.75 h was needed to obtain 98% Ph_2SiF_2 compared with 20 min in DME. This is in agreement with the earlier finding that DME was the best solvent for the silent reaction [6].

A quick and convenient method having been worked out for the synthesis of Ph_2SiF_2; the synthesis of more hindered chlorosilanes was attempted. The conversion of Ph_3SiCl (Table 1, entry 8) was complete in 1.25 h using the probe but, as the steric hindrance at silicon increased, the efficiency of the ultrasonic method decreased: Mes_2SiF_2 gave 52% yield in 4 h, $^tBu_2SiF_2$ less than 5% in 3 h, and $^tBuPh_2SiF$ 0% in 3 h (Table 1, entries 9–11). These results reflect those obtained in the silent reaction where an increase in steric hindrance at silicon also prevents rapid fluorination (Table 1, entries 8, 10 and 11).

The use of anhydrous DME (less than 0.005% H_2O) (Table 2) increased the overall rate of formation of Ph_2SiF_2, presumably by preventing formation of unwanted Si–OH-containing intermediates (Table 2, entries 1 and 2). This improvement was not found, however, either when Ph_3SiCl was sonicated with the probe (2.75 h being needed to achieve 92% conversion (Table 2, entry 3) compared with 1.25 h in reagent grade DME) or in the case of Mes_2SiCl_2 (Table 2, entry 4) (for which no reaction was detected by GLC).

Although halosilanes are moisture sensitive, the more bulky the silane the more difficult is its hydrolysis. As the presence of water had opposite effects on the yield of Ph_2SiF_2 and of Ph_3SiF or Mes_2SiF_2 it was decided to investigate the role of H_2O on the course of the reactions. The importance of a trace amount of water to accelerate the rate of heterogeneous organic reactions has been noticed previously [9]. The role of water in these reactions is to break down the crystal lattice of the inorganic salts and to produce ions, ion pairs or ion clusters which are able to react with the substrate in the organic phase. The amount of water necessary to facilitate nucleophilic substitution varies depending on the nucleophilic anion and countercation of the inorganic

Table 3
Fluorination of chlorosilanes using $(NH_4)_2SiF_6$ and water in anhydrous dimethoxyethane at room temperature

Entry	Starting material	water (ml)	Time	Yield (%)	Product
1	Mes_2SiCl_2	0.07	45 min	97 (85)	Mes_2SiF_2
				3	$Mes_2SiF(OH)$
2	Ph_3SiCl	0.07	45 min	95 (83)	Ph_3SiF
3	$^tBuPh_2SiCl$	0.20	45 min	98.5	$^tBuPh_2SiF$
				1.5	Unknown
4	$^tBu_2SiCl_2$	0.20	5 h	97 (52)	$^tBu_2SiF_2$
				3	$^tBu_2SiF(OH)$
5	$^tBu_2SiCl_2$	0.40 [a]	15 h	41	$^tBu_2SiF_2$
				18	$^tBu_2SiF(OH)$
6	$TsiSiCl_3$ [b]	0.50	24 h [c], 3 h [d]	0	—
7	$TpsiSiCl_3$ [e]	0.50	24 h [c], 3 h [d]	0	—

[a] Using Na_2SiF_6.
[b] Tsi = $(Me_3Si)_3C$.
[c] Refluxing DME.
[d] Probe at 25°C.
[e] Tpsi = $(PhMe_2Si)_3C$.

salt, as more water is needed to dissolve salts with high lattice energy, but is insensitive to the substrate structure or leaving group. It has also been found that the use of too much water lowers the yields because hydration makes the ions less reactive [9]. There is therefore an optimum amount of H_2O to use for each salt.

The results presented in Table 3 show the dramatic and surprising influence that water can have on the yields and rates of fluorination of hindered chlorosilanes in DME. The salt $(NH_4)_2SiF_6$ loses its white colour when suspended in DME and an indication of the extent of the reaction may be gained by observation of the NH_4Cl produced during the reaction as an insoluble white solid. When H_2O (70 μl) was added to the reactants (water: hexafluorosilicate molar ratio, about 4:3) used for the fluorination of Mes_2SiCl_2, the white precipitate appeared within 5 min and the reaction was complete after 45 min (Table 3, entry 1) instead of 18 h in refluxing reagent grade DME. Similarly, the fluorination of Ph_3SiCl was complete after 45 min (Table 3, entry 2). When a similar amount of H_2O was added to a stirred solution of $^tBu_2SiCl_2$ or $^tBuPh_2SiCl$ (Table 3, entries 3 and 4), the conversion started quickly (10% in 30 min for $^tBu_2SiCl_2$) but then stopped. Two further additions of water were made (total, 0.2 ml; water: salt, about 4:1 mol) to achieve complete conversion. When 0.2 ml of water was added at the beginning of the reaction, 97% of the fluoride was obtained in 5 h for $^tBu_2SiCl_2$ and 98.5% in 45 min for $^tBuPh_2SiCl$. When the amount of water was increased from 0.2 to 0.5 ml for the fluorination of $^tBu_2SiCl_2$, the amount of $^tBuSiF(OH)$ formed increased and the reaction was less effective. These last results show that a maximum reactivity is a compromise between the amount of water needed to activate the salt and the ease of hydrolysis of the chlorosilane. When the steric hindrance at silicon was further increased and $(Me_3Si)_3CSiCl_3$ or $(PhMe_2Si)_3CSiCl_3$ were used, the fluorination with addition of water (0.5 ml) gave no product (Table 3, entries 6 and 7). Attempts to fluorinate $(Me_3Si)_3CSiCl_3$ or $(PhMe_2Si)_3CSiCl_3$ were made using reflux conditions for 24 h or using the probe for 3 h; in no case could product be isolated. For these compounds the rapid decrease in the solubility of $(Me_3Si)_3CSiCl_3$ or $(PhMe_2Si)_3CSiCl_3$ when H_2O is added to the reaction mixture probably plays an important role as well as the presence of the very bulky alkyl substituents.

Finally, when $^tBu_2SiCl_2$ was stirred at room temperature with Na_2SiF_6 and 0.2 ml H_2O (Table 3, entry 5) it was shown by GLC analysis that only trace quantities of the difluorosilane had been formed after 1 h. Another 0.2 ml of H_2O was then added and the reaction left stirring overnight (total, 15 h). The GLC trace then showed the following mixture of compounds: 41% $^tBu_2SiCl_2$; 18% $^tBu_2SiF(OH)$; 41% $^tBu_2SiF_2$. This difference in reactivity between $(NH_4)_2SiF_6$ and Na_2SiF_6 may be accounted for in terms of their solubilities in water which, at 17°C, are 18.16 and 0.652 g l^{-1} respectively [10].

3. Conclusion

The fluorination of bulky silanes with hexafluorosilicate salts in DME is dependent on the salt used and on the size of the substituents in the substrate. The rate of fluorination of sterically hindered silanes is greatly increased by ultrasound under anhydrous conditions at room temperature. However, as the substrate gets more and more bulky, its reactivity decreases and the use of ultrasound is not sufficient to cause a reaction to occur. Addition of water to stirred fluorination mixtures of bulky chlorosilanes also causes rate increases and $^tBu_2SiCl_2$ gives the corresponding difluoride in only 5 h at room temperature whereas 2 weeks at reflux are required under anhydrous conditions.

4. Experimental section

All reactions involving a bath were carried out in a rectangular Pulsatron 125H ultrasonic cleaner from Kerry Ultrasonics using a frequency 38 kHz ± 10%. All reactions in the bath were carried out in round-bottomed flasks or Schlenk tubes and the reaction vessel was placed in the position of maximum intensity (or agitation in the reaction vessel) which was generally found to be between the two transducers, in the centre of the cleaning tank. Temperature control for reactions in the bath was achieved by periodic change of the water giving the following temperature accuracy: $T \pm 3$°C. In all cases the water level was kept between 2 and 4 cm below the top level of the tank, depending on the activity visible in the reaction vessel.

The ultrasonic probe used was a Sonic and Materials VC 300 sonifier consisting of a 20 kHz ultrasound generator, with a variable power output up to 300 W. This was kept in a sound proof box and all reactions were carried out in the dark. A horn of 12 mm diameter at the radiating surface was used and the apparatus was equipped with a joint to allow sonication under an inert atmosphere in glass vessels. A Suslick cell (15 ml) was used for all reactions using the probe and temperature control was carried out by immersing the reaction vessel, fitted to the probe, partially into a coolant. The solvent inside the sonicated vessel was generally found to be at a temperature between 20 and 30°C higher than that of the coolant, depending on the ultrasound intensity used.

THF was heated under reflux with sodium wire and benzophenone until a deep-purple colouration was obtained and was freshly distilled before use. Reagent grade and anhydrous DME were obtained from the Aldrich Chemical Company and were used as received.

The ^{19}F and ^{29}Si NMR spectra were recorded at 84.6 and 59.6 MHz respectively on a JEOL EX-90 FT-NMR spectrometer. ^{19}F and ^{29}Si chemical shifts are relative to $CFCl_3$ and tetramethylsilane respectively. Analyses by GLC were recorded on a Perkin–Elmer 8320 capillary GLC instrument with a flame ionization detector and a 25 m non-polar BP1 column. Mass spectra were obtained by chemical ionization (NH_3) or electron impact (EI) at 70 eV on a Finnigan 4500 quadrupole mass spectrometer. For analysis by linked GLC–mass spectrometry (MS) a Varian GC 3400 gas chromatograph with a 25 m BP1 non-polar column was used

For each of the reactions the $(NH_4)_2SiF_6$ and Na_2SiF_6 were dried prior to use by warming the white solid at 80°C under vacuum and then stored under argon.

4.1. Reactions under reflux

The chlorosilane (2.9 mmol), the hexafluorosilicate (6.0 mmol) and the solvent (30 ml) were charged in a 50 ml flask equipped with a magnetic stirrer bar, condenser and argon inlet tube. The heterogeneous mixture was heated to reflux and the reaction monitored by GLC. The experiment was stopped upon complete disappearance of the starting material. The mixture was then concentrated under reduced pressure prior to addition of 15 ml of diethyl ether and filtration. Removal of the solvents by rotary evaporator gave the fluorinated product or, when no reaction had occurred, the starting material was recovered.

4.2. Reactions using the cleaning bath

The chlorosilane (2.9 mmol), the hexafluorosilicate (6.0 mmol) and the solvent (30 ml) were introduced into 100 ml Schlenk tube under a stream of argon. The heterogeneous mixture was positioned in a cleaning bath at 20°C for best agitation inside the flask and the sonication started. The course of the reaction was monitored by GLC and the experiment was stopped upon complete disappearance of the starting material. The reaction mixture was then concentrated under reduced pressure prior to addition of 15 ml of diethyl ether and filtration. Removal of the solvents by rotary evaporator gave the fluorinated product.

4.3. Reactions using the probe

To a 15 ml reactor under argon charged with the hexafluorosilicate (1.5 mmol) and fitted to the probe was added the chlorosilane (1.5 mmol) in the solvent (15 ml). The mixture was cooled by an ice–water slush bath and the sonication started on power setting 7. The course of the reaction was monitored by GLC and the experiment was stopped upon complete disappearance of the chlorosilane. The reaction vessel was then removed from the probe and the mixture concentrated under reduced pressure prior to addition of 10 ml of diethyl ether. The mixture was filtered to remove the ammonium salt and the salt washed with Et_2O (2 ml). Removal of the combined solvents by rotary evaporator gave the desired products.

4.4. Reactions using a trace amount of water in dimethoxyethane

The chlorosilane (1.5 mmol), the hexafluorosilicate (3.0 mmol) and the solvent (10 ml) were charged in a 50 ml round-bottomed flask equipped with a magnetic stirrer bar and an argon inlet tube. The heterogeneous mixture was stirred at room temperature and the H_2O in DME (5 ml) added dropwise over a period of 10 min. The course of the reaction was monitored by GLC and the experiment was stopped upon complete disappearance of the starting material. The mixture was concentrated to a third of its volume under reduced pressure prior to addition of 15 ml of diethyl ether and drying over $MgSO_4$. After filtration, removal of the solvents by rotary evaporator gave the desired product.

4.5. Identification of products

The following data were used to identify the products in the various reactions.

Mes$_2$SiF$_2$: ^{19}F NMR ($CDCl_3$): δ −124.9 (J_{SiF} = 302 Hz, J_{HF} = 2 Hz) ppm. ^{29}Si NMR ($CDCl_3$) δ −22.9 (t, J_{SiF} = 302 Hz) ppm. MS (EI): *m/z* 304 (33%, $[M]^+$), 289 (70, $[M-Me]^+$), 185 (22, $[M-Mes]^+$), 120 (100, $[MesH]^+$), 105 (92, $[MesH-Me]^+$) 91 (56, $[C_6H_4Me]^+$).

Ph$_2$SiF$_2$: ^{19}F NMR (DME): δ −144.2 (J_{SiF} = 292 Hz, d, J_{HF} = 3.1 Hz) ppm. ^{29}Si NMR (DME): δ −23.74 (t, J_{SiF} = 292 Hz) ppm. MS (EI): *m/z* 220 (100, $[M]^+$), 199 (19, $[M-HF-H]^+$), 154 (85, $[Ph_2]^+$), 77 (100, $[Ph]^+$).

Ph$_2$SiF(OH): ^{19}F NMR (DME): δ −142.9 ppm. ^{29}Si NMR shift not recorded.

Ph$_3$SiF: ^{19}F NMR (DME): δ −170.4 (J_{SiF} = 281.4 Hz) ppm. ^{29}Si NMR (DME): δ 4.35 (J_{SiF} = 281.4 Hz) ppm. MS (EI): *m/z* 201 (90, $[M-Ph]^+$), 154 (100, $[Ph_2]^+$).

^{t}Bu$_2$SiF$_2$: ^{19}F NMR (DME): δ −158.9 (J_{SiF} = 325 Hz) ppm. ^{29}Si NMR (DME): δ −8.51 (J_{SiF} = 325 Hz) ppm.

^{t}Bu$_2$SiF(OH): ^{19}F NMR (DME): δ −158.6 (J_{SiF} = 325 Hz) ppm. ^{29}Si NMR shift not recorded.

^{t}BuPh$_2$SiF: ^{19}F NMR (DME): δ −184.1 (J_{SiF} = 290 Hz) ppm. ^{29}Si NMR (DME): δ 3.51 (d, J_{SiF} = 290 Hz) ppm. MS (EI): *m/z* 258 (12, $[M]^+$), 201 (100, $[M-Bu]^+$), 182 (8, $[Ph_2Si]^+$), 47 (40, $[SiF]^+$).

Acknowledgements

We wish to thank the university of Salford Research Fund for financial support (to R.L.) and the FMC Corporation (Lithium Division) for a gift of chlorosilanes.

References

[1] R. Damrauer and S.E. Danahey, *Organometallics 5* (1986) 1990.
[2] Y. Nakadaira and H. Sakurai, *J. Organomet. Chem, 309* (1986) 247.
[3] M. Weidenbruch and K. Kramer, *J. Organomet. Chem, 291* (1985) 159.
[4] R.J.P. Corriu, C. Guerin, B.J.L. Henner and W.W.C. Won Chi Man, *Organometallics, 7* (1988) 237.
[5] R.M. Pike and K. Koziski, *J. Organomet. Chem. Libr., 9* (1980) 41.
[6] R. Damrauer, R.A. Simon and B. Kanner, *Organometallics, 7* (1988) 1161.
[7] S.V. Ley and C.M.R. Low, *Ultrasound in Synthesis*, Springer, Berlin, 1989; K.S. Suslick (ed.), *Ultrasound, Its Chemical, Physical and Biological Effects*, VCH, Weinheim, 1988; T.J. Mason and J.P. Lorimer, *Sonochemistry, Theory, Applications and Uses of Ultrasound in Chemistry*, Ellis Horwood, Chichester, West Sussex, 1988.
[8] L.D. Rozenberg, *Ultrason. News, 4* (1960) 4, cited in K.S. Suslick (ed.), *Ultrasound: Its Chemical, Physical and Biological Effects*, VCH, Weinheim, 1988.
[9] T. Ando and T. Kimura, *Adv. Sonochem., 2* (1991) 211.
[10] R.C. Weast (ed.), *Handbook of Chemistry and Physics*, Chemical Rubber Company, West Palm Beach, FL, 59th edn., 1978–1979.