Synthesis of (trichloromethyl)organosilanes by catalytic decarboxylation of (trichloroacetoxy)organosilanes

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A method for preparing (trichloromethyl)organosilanes by the catalytic decarboxylation of the corresponding trichloroacetoxysilanes $RMe_2SiOC(O)CCl_3$ (R = Me, $ClCH_2$, Ph, Me_3Si, and H) has been developed. The method involves heating the starting compounds without a solvent in the presence of a catalyst (quaternary ammonium salts or potassium salts with the addition of crown ethers). Tertiary amines (Et_3N, Bu_3N) catalyze this reaction only when heating is carried out in donor aprotic solvents (THF, acetonitrile) in the presence of oxygen. Thermal decomposition of (trichloroacetoxy)organosilanes, in contrast to catalytic decarboxylation, begins at a higher temperature and yields a mixture of products.

Key words: organosilanes, trichloroacetoxy and trichloromethyl derivatives; catalytic decarboxylation.

(Trichloromethyl)organosilanes are still not easily accessible compounds, despite the fact that some representatives of this class were prepared quite long ago. Several useful properties of (trichloromethyl)organosilanes, such as their ability to generate dichlorocarbene[1] and the trichloromethanide anion[2] under mild conditions, are known; in addition, these compounds can be used as agrochemical preparations that differ beneficially from their predecessors (like DDT) in that they do not accumulate in the environment owing to the tendency of the Si—CCl_3 bond to undergo slow hydrolysis.[3] Attempts to synthesize silicon-containing analogs of DDT have been undertaken,[4] however, an extensive search has not been possible due to limitations of the existing synthesis methods. For example, direct chlorination of methylchlorosilanes[5] and cleavage of polychlorodisilanes in CCl_4 through the action of bases[6] allow one to prepare trichloromethyl derivatives containing Si—Cl bonds, which cannot be subjected to selective alkylation.[7] Other known methods are either rather cumbersome (the use of CCl_3Li at temperatures ≤ -100 °C)[8] or involve the use of expensive organophosphorus compounds, *viz.*, hexametapol[9] and tris(diethylamino)phosphine,[10] as solvents or reagents.

Results and Discussion

The facile and convenient method for preparing (trichloromethyl)organosilanes developed by us is based on the catalytic decarboxylation of the corresponding silyl trichloroacetates. The reaction occurs at 100—110 °C without a solvent in the presence of 0.005 equiv. of a catalyst (reaction (1)).

$$\mathrm{RMe_2SiOC(O)CCl_3} \xrightarrow[\Delta]{\mathrm{Cat}} \mathrm{RMe_2SiCCl_3} + \mathrm{CO_2} \qquad (1)$$

$$\mathrm{R = Me,\ ClCH_2,\ Ph,\ Me_3Si,\ H}$$

We used quaternary ammonium salts — benzyltriethylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium fluoride (hydrate) — and also potassium salts (K_2CO_3 and KF) in the presence of the complex of 18-crown-6 with acetonitrile (18-C-6 · MeCN) as catalysts. In terms of their effectiveness, the catalysts can be arranged in the following sequence: $Et_3(PhCH_2)NCl \approx Bu_4NBr > K_2CO_3/\text{18-C-6} \cdot MeCN > Bu_4NF \cdot H_2O > KF/\text{18-C-6} \cdot MeCN \gg Me_4NBr$, Me_4NI. The salts soluble in trichloroacetoxysilanes, *viz.*, Bu_4NBr and $Et_3(PhCH_2)NCl$, turned out to be the most effective. Tetrabutylammonium fluoride smoothly catalyzes decarboxylation when conversion is no more than 50 %. After this, side decomposition processes accompanied by blackening of the reaction mixture are observed, and this results in a decrease in the yields of the products. A similar situation occurs when potassium fluoride in the presence of 18-C-6 · MeCN is used as the catalyst. Tetramethylammonium halides are inefficient due to their poor solubility in trichloroacetoxysilanes. The preparative yields of (trichloromethyl)organosilanes were 70—90 % with Bu_4NBr or $Et_3(PhCH_2)NCl$ as the catalyst (Table 1). In the case of potassium carbonate in combination with the crown-ether, the yields of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 150—153, January, 1995.

Table 1. Characteristics of the trichloroacetoxysilanes and trichloromethylsilanes synthesized

Compound		Yield (%)	B.p./°C (p/Torr) [M.p.]	n_D^{20}	d_4^{20}	Found/Calculated (%) C	H	Si	Cl	Molecular formula
$ClCH_2Me_2SiOC(O)CCl_3$	**1**	54	92(0.1)	1.4655	1.3522	22.11 22.24	3.13 2.99	10.58 10.40	52.44 52.52	$C_5H_8SiO_2Cl_4$
$HMe_2SiOC(O)CCl_3$	**2**	72	63(20)	1.4459	1.2007	22.00 21.68	3.38 3.18	12.55 12.68	48.01 48.01	$C_4H_7SiO_2Cl_3$
$PhMe_2SiOC(O)CCl_3$	**3**	76	139(0.5)	1.5100	1.2867	40.22 40.35	3.65 3.73	9.57 9.44	35.91 35.73	$C_{10}H_{11}SiO_2Cl_3$
$Me_5Si_2OC(O)CCl_3$	**4**	70	87(0.1)	1.4653	1.1355	28.70 28.60	5.20 5.15	19.05 19.12	36.30 36.20	$C_7H_{15}Si_2O_2Cl_3$
$ClMe_2SiOC(O)CCl_3$	**5**	20[a]	53(0.1)	1.4573	1.4275	18.92 18.77	2.27 2.36	11.06 10.97	55.53 55.40	$C_4H_6SiO_2Cl_4$
$Me_2Si(OC(O)CCl_3)_2$	**6**	55	127(0.1)	1.4687	1.5160	18.75 18.82	1.54 1.58	7.26 7.33	55.48 55.55	$C_6H_6SiO_4Cl_6$
$(CCl_3CO_2SiMe_2)_2$	**7**	50	120(0.1)	1.4829	1.3837	21.83 21.79	2.68 2.74	12.76 12.74	48.20 48.23	$C_8H_{12}Si_2O_4Cl_6$
$ClCH_2SiMe_2CCl_3$	**8**	75[b] (78)[c]	[70—72]	—	—	21.51 21.26	4.01 3.57	12.39 12.43	62.90 62.75	$C_4H_8SiCl_4$
HMe_2SiCCl_3	**9**	34[e] (40)[c]	40(20) [30—32]	—	—	20.42 20.30	3.76 3.97	15.55 15.82	59.89 59.91	$C_3H_7SiCl_3$
$PhMe_2SiCCl_3$	**10**	77[b] (75)[c]	80(0.05) [20]	1.5415	1.2339	42.58 42.62	4.42 4.37	11.16 11.07	42.08 41.93	$C_9H_{11}SiCl_3$
$Me_3SiSiMe_2CCl_3$	**11**	73[b] (70)[c]	46(0.1) [23—24]	1.4846[f]	1.0900[g]	29.01 28.86	6.20 6.05	22.34 22.49	42.37 42.59	$C_6H_{15}Si_2Cl_3$

[a] Undergoes partial disproportionation to give Me_2SiCl_2 and compound **6**. [b] Bu_4NBr and $(PhCH_2)Et_3NCl$ as the catalyst. [c] Yield of the product of the decarboxylation of the corresponding trichloroacetoxysilane in THF (65 °C) in the presence of Et_3N. [d] K_2CO_3/18-C-6 · MeCN as the catalyst. [e] Lit.[8]: b.p. 134—138 °C (760 Torr). [f] At 25 °C.

(trichloromethyl)organosilanes are not lower, however, the reaction proceeds somewhat more slowly.

The starting (trichloroacetoxy)organosilanes were prepared according to reaction (2) by boiling commercially available organochlorosilanes and trichloroacetic acid in chlorohydrocarbons ($CHCl_3$, CCl_4, 1,2-$C_2H_4Cl_2$) for 8 h.

$$RMe_2SiCl + CCl_3CO_2H \xrightarrow[\Delta]{CCl_4} \underset{\mathbf{1-7}}{RMe_2SiOC(O)CCl_3} + HCl \qquad (2)$$

(Trichloroacetoxy)organosilanes **1—7** thus prepared (Tables 1 and 2) are stable colorless liquids sensitive to air moisture. At a high temperature without a catalyst they slowly decompose to yield a complex mixture of dark-colored products. For example, when compound **1** was heated in an evacuated tube for 6 h at 230 °C, it decomposed by 47 % (reaction (3)).

$$\underset{\mathbf{1}}{ClCH_2Me_2SiOC(O)CCl_3} \xrightarrow{\Delta} \underset{\mathbf{8}}{ClCH_2Me_2SiCCl_3} + \qquad (3)$$
$$+ ClCH_2Me_2SiCl + CHCl_3 + CO_2 + ...$$

Chloromethyl(dimethyl)trichloromethylsilane (**8**) is formed in a low yield (9 %). Decomposition also gave chloromethyl(dimethyl)chlorosilane (31 %), CO_2, $CHCl_3$, and a number of compounds that we were not able to identify. Thermal decomposition of pentame-

Table 2. ^1H NMR spectra of the compounds synthesized

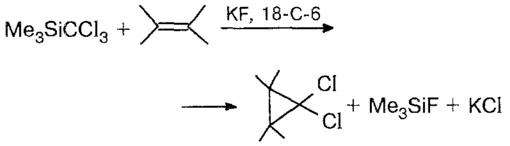
Compound	Group	δ	$^2J_{^{29}Si,^1H}$/Hz
1	Me_2Si $ClCH_2$	0.52 3.03	7.14 4.23
2	Me_2Si H—Si	0.47 4.92	7.47 224.40 (^1J)
3	Me_2Si Ph	0.75 7.40—7.80	7.04
4	Me_3Si Me_2Si	0.17 0.43	6.71 6.29
5	Me_2Si	0.74	
6	Me_2Si	0.72	6.76
7	Me_2Si	0.62	
8	Me_2Si $ClCH_2$	0.50 3.09	6.95 4.04
9	Me_2Si H—Si	0.44 4.33	7.18 210.00 (^1J)
10	Me_2Si Ph	0.82 7.40—8.00	6.76
11	Me_3Si Me_2Si	0.21 0.38	6.67 6.24

thyltrichloroacetoxydisilane (**4**) (converted by 69 % over a period of 6 h at 220 °C) results in a more complex mixture of products (reaction (4)).

$$\underset{\mathbf{4}}{Me_5Si_2OC(O)CCl_3} \xrightarrow[\Delta]{} Me_5Si_2CCl_3 + Me_5Si_2Cl + Me_3SiOC(O)CCl_3 + Me_3SiCl + CHCl_3 + CO_2 + \ldots \quad (4)$$

In addition to the expected products, *viz.*, $Me_5Si_2CCl_3$ (11 %), Me_5Si_2Cl (25 %), $CHCl_3$, and CO_2, we also detected trimethyltrichloroacetoxysilane (18 %) and trimethylchlorosilane (5 %). The two latter compounds are apparently formed through cleavage of the Si—Si bond. Data on analogous thermal transformations of disilanyl acetates have been published previously.[11] Thus, although (trichloromethyl)organosilanes are formed by the thermolysis of the corresponding silyl trichloroacetates, their yields are low and it is difficult to purify them. The use of nucleophilic catalysts allows one to lower the temperature of decarboxylation by more than 100 °C and to considerably increase the yields of (trichloromethyl)organosilanes.

It should be noted that subsequent catalytic transformations of decarboxylation products involving cleavage of the $Si—CCl_3$ bond are, in principle, possible. For example, it is known that through the action of fluoride ions under mild conditions[1] (25 °C, diglyme), trimethyl(trichloromethyl)silane yields dichlorocarbene, which has been identified based on the product of its cyclopropanation (reaction (5)).



(5)

However, this reaction is rather prolonged (24 h and more) and requires a highly ionizing solvent and an equimolar amount of fluoride. Decarboxylation of trichloroacetoxysilanes, which occurs in the presence of 0.005 equiv. of a catalyst, is obviously a much faster process than the replacement of the trichloroacetoxy group (in the starting compounds) or the replacement of the trichloromethyl group (in the products) by the active anion of a catalyst, otherwise its deactivation would be observed.

Tertiary amines are inactive in the decarboxylation of trichloroacetoxysilanes if it is carried out without a solvent. When a mixture of trimethyltrichloroacetoxysilane with tributylamine is kept at 100 °C for a long time, resinification of the reaction mixture is the predominant process. However, an example of decarboxylation of trimethyltrichloroacetoxysilane in the presence of tertiary amines carried out in THF at 65 °C over a period of 8 h (reaction (6)) has been reported.[12]

$$Me_3SiOC(O)CCl_3 \xrightarrow[\Delta]{Et_3N/THF} Me_3SiCCl_3 + CO_2 \quad (6)$$

By using this method we managed to prepare (trichloromethyl)silanes **8**—**11** with various substituents at the Si atom (see Tables 1 and 2). When decarboxylation was completed, the yield of dimethyl(trichloromethyl)silane (**9**) was 85 % (according to GLC), but in the course of its isolation in the pure state, the yield decreased somewhat due to the side reactions of self-reduction in the presence of amine (reaction (7)).

$$\underset{\mathbf{9}}{HMe_2SiCCl_3} \xrightarrow[\Delta]{Et_3N} Cl_2CHSiMe_2Cl + ClCH_2SiMe_2Cl + Me_3SiCl \quad (7)$$

Prolonged storage of compound **9** containing slight amounts of amine, at 20 °C also affords a mixture of chlorosilanes, however, pure dimethyl(trichloromethyl)silane is relatively stable. We also managed to obtain compound **9** in a satisfactory yield by decarboxylation of dimethyltrichloroacetoxysilane without a solvent in the presence of potassium carbonate and the 18-C-6 • MeCN complex. The use of quaternary ammonium salts as catalysts was inefficient in this case, probably due to the fact that the catalyst decomposes at a lower temperature than that necessary for decarboxylation.

The resulting (trichloromethyl)organosilanes are more stable than the corresponding trichloroacetoxysilanes. In fact, compounds **1** and **4** decompose at noticeable rates at 230 °C and 220 °C, respectively (see reactions (3) and (4)), whereas the products of their decarboxylation, silanes **8** and **11**, remain unchanged at these temperatures.

Compounds **6** and **7**, which contain two trichloroacetoxy groups each, are also decarboxylated in the presence of tertiary amines in THF (or without a solvent in the presence of quaternary ammonium salts). However, these reactions are accompanied by undesired side condensation and resinification of the reaction mixture and cannot be used for synthetic purposes.

We also studied in detail the decarboxylation of trichloroacetoxysilanes in the presence of tertiary amines in a solvent. In particular, it was shown that the reaction occurs at a noticeable rate only in the presence of oxygen. When decarboxylation was carried out without protection from oxygen, the reaction was zero order with respect to silane and first order with respect to amine. The characteristic features and mechanism of this interesting reaction will be reported in subsequent communications.

Experimental

The ^1H NMR spectra were recorded on a Tesla BS-487-C spectrometer (80 MHz) in $CDCl_3$ using $CHCl_3$ as the internal standard. GLC analysis was carried out on a Tsvet-500 chromatograph (a 0.4×200 cm stainless-steel column packed with 5 % SE-30 on Chromaton-N-Super, a heat-conductivity detector, helium as the carrier gas).

The solvents were purified by standard methods: THF was distilled over metallic Na (prior to this, it was treated with KOH), then over $LiAlH_4$. Chlorohydrocarbons were distilled over P_2O_5.

Synthesis of (trichloroacetoxy)organosilanes (1—5) and bis(trichloroacetoxy)silanes (6, 7) (general procedure). A mixture of the corresponding monochlorosilane (0.3 mol) and trichloroacetic acid (0.3 mol) in 200 mL of anhydrous chloroform or $1,2\text{-}C_2H_4Cl_2$ was boiled for 16 h. When the reaction was completed (evolution of HCl ceased) the solvent was evaporated, and the residue was fractionated *in vacuo*. For bis(trichloroacetoxy)silanes **6** and **7**, a threefold molar excess of trichloroacetic acid was used.

Catalytic decarboxylation of trichloroacetoxysilanes 1—5. Trichloroacetoxysilane (0.1 mol) and a catalyst ($5 \cdot 10^{-4}$ mol) (for the optimal catalyst, see Table 1) were placed in a flask equipped with a stirrer, a reflux condenser, and a thermometer. The reaction mixture was heated on an oil bath with intense stirring while the temperature was maintained in the range 100—110 °C. The course of decarboxylation was monitored by GLC and volumetry. The reaction was completed after a period of 30—40 min when it was catalyzed by quaternary ammonium salts, or after a period of 1.5 h when K_2CO_3 or KF were used. The reaction products were dissolved in 40 mL of hexane, washed with conc. H_2SO_4 (2×10 mL) in the cold to remove the unreacted starting trichloroacetoxysilane, then washed with water, and dried with anhydrous Na_2SO_4. Removal of hexane gave virtually pure product, which was additionally distilled or sublimed *in vacuo* if necessary (see Table 1).

Thermal decomposition of trichloroacetoxysilanes was carried out in evacuated tubes at 220—230 °C. The products were identified by GLC. It was shown in control runs that all of the monotrichloroacetoxysilanes are stable under the conditions of GLC analysis (100—170 °C).

Synthesis of (trichloromethyl)organosilanes by decarboxylation of trichloroacetoxysilanes in the presence of tertiary amines was carried out by a procedure similar to that described previously[12] for preparing trimethyl(trichloromethyl)silane. THF and acetonitrile were used as solvents, Et_3N was used as the catalyst (0.25—0.30 mol L^{-1}).

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Received May 10, 1994;
in revised form June 16, 1994