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Preliminary communication

THE PREPARATION OF (DICHLOROMETHYL)SILANES UNDER PHASE TRANSFER CONDITIONS

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Summary

The synthesis of (dichloromethyl)silanes via the phase transfer catalyzed decomposition of sodium trichloroacetate in the presence of an organosilane is described.

In our interest in the chemistry of (dichloromethyl)silanes [1] we sought a general route to these systems which could be carried out on a reasonably large scale and in reasonable yield. Two general routes to this class of compounds have been reported, namely the reaction of (dichloromethyl)lithium with chlorosilanes [2] and the insertion of dichlorocarbene into a silicon hydrogen bond (eq. 1, 2).

$$R_3SiCl + LiCHCl_2 \xrightarrow[-90^\circ C]{THF} R_3SiCHCl_2 \qquad (1)$$

$$R_3SiH + \text{“}{:}CCl_2\text{”} \longrightarrow R_3SiCHCl_2 \qquad (2)$$

We chose to investigate the dichlorocarbene insertion pathway, a route which has been reported employing sodium trichloroacetate [3], (trichloromethyl)phenylmercury [2], (bromodichloromethyl)phenylmercury [4], (iododichloromethyl)phenylmercury [5], (bromodichloromethyl)cyclohexylmercury [6] and (trichloromethyl)cyclohexylmercury [6] as dichlorocarbene sources.

Our first attempts were to employ the phase transfer approach of Makosza [7] to generate the dichlorocarbene in the presence of the silane. This results in hydrolysis of the silane, and is of no use in the preparation of (dichloromethyl)silanes (eq. 3) [8].

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$$\mathrm{Et_3SiH + CHCl_3 \xrightarrow[Q^+X^-]{NaOH} Et_3SiOSiEt_3} \qquad (3)$$

Based on some early work of Seyferth and coworkers [3], who prepared (dichloromethyl)triethylsilane in 32% yield from sodium trichloroacetate in glyme and on some recent work by Dehmlow [9] and Idemori and coworkers [10] we decided to investigate the phase transfer catalyzed decomposition of sodium trichloroacetate in the presence of organosilanes as a potential route to (dichloromethyl)silanes.

Refluxing equal molar amounts of triethylsilane and sodium trichloroacetate in toluene containing 10 mole percent of 18-crown-6 showed a gradual formation of (dichloromethyl)triethylsilane to a maximum of about 30% conversion as estimated by NMR spectroscopy. The addition of 2 equivalents more of the salt resulted in about 70% conversion, again by NMR (eq. 4). A simpler approach was to use three equivalents of sodium trichloroacetate from the outset of the reaction. Interestingly, the reaction did not proceed using potassium trichloroacetate with 18-crown-6 as the dichlorocarbene source even though the salt was scrupulously dried. Catalysts other than 18-crown-6 were also effective. For example, one molar equivalent of polyethylene glycol 200 worked almost as well, although PEG 400 did not work in our hands. In addition, the use of tetrabutylammonium bisulfate in chloroform gave a 48% yield of (dichloromethyl)triethylsilane. Finally, it is important to note that the reaction of 3 equivalents of sodium trichloroacetate with triethylchlorosilane in DME gave only 7% (NMR) of (dichloromethyl)triethylsilane. Thus, an excess of the silane seems to be better in this procedure [3]. The results are given in Table 1.

$$\mathrm{Et_3SiH + Cl_3CCO_2Na \xrightarrow[toluene/reflux]{18\text{-}crown\text{-}6} Et_3SiCHCl_2} \qquad (4)$$

It is of interest to point out that (+)-α-naphthylphenylmethylsilane was converted to (+)-(dichloromethyl)-α-naphthylphenylmethylsilane in 70%

TABLE 1

PRODUCTS AND YIELDS OF THE REACTION OF SILANES WITH SODIUM TRICHLOROACETATE UNDER PHASE TRANSFER CATALYSIS

Silane	Product	Yield (%) [a]
$\mathrm{Et_3SiH}$	$\mathrm{Et_3SiCHCl_2}$ [b]	62
$\mathrm{Et_3SiH}$	$\mathrm{Et_3SiCHCl_2}$ [c]	48
$\mathrm{Et_3SiH}$	$\mathrm{Et_3SiCHCl_2}$ [d]	55 [e]
$\mathrm{Et_3SiH}$	$\mathrm{Et_3SiCHCl_2}$	7 [f]
$\mathrm{PhMe_2SiH}$	$\mathrm{PhMe_2SiCHCl_2}$ [b]	49
$\mathrm{Ph_2MeSiH}$	$\mathrm{Ph_2MeSiCHCl_2}$ [b]	50
$\mathrm{Ph_2SiH_2}$	$\mathrm{Ph_2HSiCHCl_2}$ [b]	26 [g]
(+)-α-NpPhMeSiH	(+)-α-NpPhMeSiCHCl$_2$ [b]	70 [h]

[a] Isolated yield. [b] 0.5 *M* in toluene with 10 mole percent 18-crown-6. [c] In chloroform with 10 mole percent tetrabutylammonium bisulfate. [d] 0.5 *M* in toluene with 100 mole percent PEG 200. [e] NMR analysis. [f] Three equivalents of sodium trichloroacetate in DME. [g] None of the bis(dichloromethyl)diphenylsilane was observed by NMR. [h] α_D^{25} + 23.07 (2.12 hexane) corresponding to 100% optical purity [2].

yield and 100% optical purity with predominant retention of configuration at silicon. This is consistent with the results of Sommer et al. [2].

The preparation of (dichloromethyl)dimethylphenylsilane is representative. A 50 ml, 3-necked flask, equipped with magnetic stirrer, condenser and nitrogen inlet was charged with 1.36 g (10 mmol) of dimethylphenylsilane, 0.26 g (1 mmol) of 18-crown-6 and 5.54 g (30 mmol) of sodium trichloroacetate (dried under vacuum at 120°C) in 20 ml of dry toluene. The reaction mixture was heated to reflux for 6 h, cooled, filtered through celite, washed with water and dried over Na_2SO_4. The solvent was removed at reduced pressure and the residue distilled to give 1.0 g (49%) of the product; b.p. 99–100°C/1.9 mmHg; n_D^{26} 1.5305.

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