Journal of Organometallic Chemistry, 277 (1984) 47-52
Elsevier Sequoia S.A., Lausanne - Printed in The Netherlands

REACTIONS OF TELLURIUM(IV) CHLORIDES WITH SOME ORGANOSILICON HYDRIDES

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(Received April 24th, 1984)

Summary

The reactions of several organosilicon hydrides Ph_nSiH_{4-n}, $n = 1, 2$; R_3SiH, $R_3 = Ph_3$, Ph_2Me, $PhMe_2$, $(n\text{-}C_6H_{13})_3$; $(p\text{-}Me_2HSi)_2C_6H_4$, with $TeCl_4$ in benzene resulted in the formation of tellurium metal and chlorosilanes in 75–90% yields. Similar reactions with aryltellurium trichlorides ($RTeCl_3$, R = Ph, p-$MeOC_6H_4$, p-$EtOC_6H_4$) proceeded in two different ways. On stirring at room temperature for 6–8 h, diaryl ditellurides and chlorosilanes were obtained in 70–95% yields whereas on refluxing for 6–10 h, tellurium powder and diaryltellurium dichlorides were obtained along with the chlorosilanes in 80–95% yields. Diaryltellurium dichlorides (R_2TeCl_2, R = Ph, p-$MeOC_6H_4$) did not react readily with $PhSiH_3$ nor with Ph_3SiH.

Introduction

$TeCl_4$ and $RTeCl_3$ are known to act both as chlorinating and tellurating agents [1–12]. For example, $TeCl_4$ reacts with olefins to give monochloro or dichloro derivatives as the major products via addition [2–8], whereas with aromatic compounds bearing activating substituents, it gives *para*-substituted $RTeCl_3$ and R_2TeCl_2 via electrophilic aromatic substitution [9–12]. With unactivated aromatic compounds, anhydrous aluminum trichloride needs to be present [13]. $TeCl_4$ and $RTeCl_3$ also react with arylsilicon compounds in a similar way to give *para* substituted condensation products if the substituent on the aromatic ring is activating [14] or electrophilic aromatic substitution at the *ipso* position if the silyl substituent is directly bonded to the phenyl ring [15]. As an extension of our work on the reactions of organosilicon compounds with tellurium(IV) chlorides [14,16], we describe here the reactions with various organosilicon hydrides in which the tellurium compounds are reduced in the process of chlorinating the silicon hydrides.

0022-328X/84/$03.00

Results and discussion

Tellurium tetrachloride and organosilicon hydrides react as shown in eq. 1.

$$Ph_2SiH_2 + TeCl_4 \xrightarrow[\text{reflux}]{\text{benzene}} Ph_2SiCl_2 + Te + 2HCl \quad (1)$$

The reactants were refluxed in benzene for 2–6 h; the reaction monitored by ^1H NMR spectroscopy was complete when the Si–H proton signal had disappeared. The evolution of two equivalents of HCl gas was confirmed by carrying out the reaction on a vacuum line, condensing the HCl into a liquid nitrogen trap and taking the IR spectrum of the evolved gas. Other silanes reacted similarly to Ph_2SiH_2 under conditions summarised in Table 1. Removal of tellurium from the solution by filtration and evaporation of the filtrate gave pure chlorosilanes. The experimental work-up was very simple and the yields were good. An excess of $TeCl_4$ made it difficult to separate chlorosilanes from the reaction mixture because of the slow deposition of tellurium metal from $TeCl_2$ which is probably the intermediate in the reduction of $TeCl_4$ to tellurium. There was no indication of evolution of hydrogen as reported in a similar reaction between $TeCl_4$ and Et_3SiH [17] for which the products were claimed to be Et_3SiCl and hydrogen and a trace of HCl.

The reaction between organosilicon hydrides and aryltellurium trichlorides were carried out in two ways. When the reactants in 3/4 mole ratio were stirred at room temperature for 6–8 h, diaryl ditelluride and chlorosilanes were obtained according to eq. 2.

$$3Ph_2SiH_2 + 4p\text{-}MeOC_6H_4TeCl_3 \xrightarrow[\text{6 h}]{\text{stir r.t}} 3Ph_2SiCl_2 + 2(p\text{-}MeOC_6H_4)_2Te_2 + 6HCl \quad (2)$$

Of the many examples studied, only the reaction between p-$EtOC_6H_4TeCl_3$ and Ph_2SiH_2 needed refluxing for 4 h to yield the ditelluride (eq. 2). The ditellurides were separated by column chromatography because both of the products are highly

TABLE 1

REACTIONS OF $TeCl_4$ WITH VARIOUS ORGANOSILICON HYDRIDES IN BENZENE

No	Reactants	Mole ratio	Silicon product [a]	Reflux time (h)	Yield (%)
1	$TeCl_4 + PhSiH_3$	1/1	$PhSiHCl_2$	5	75
2	$TeCl_4 + PhSiH_3$	3/2	$PhSiCl_3$	6	75
3	$TeCl_4 + Ph_2SiH_2$	1/1	Ph_2SiCl_2	3	95
4	$TeCl_4 + PhMeSiH_2$	1/1	$PhMeSiCl_2$	4.5	90
5	$TeCl_4 + Ph_3SiH$	1/2	Ph_3SiCl	2.5	95
6	$TeCl_4 + Ph_2MeSiH$	1/2	$Ph_2MeSiCl$	4	80
7	$TeCl_4 + PhMe_2SiH$	1/2	$PhMe_2SiCl$	4	95
8	$TeCl_4 + (n\text{-}C_6H_{13})_3SiH$	1/2	$(n\text{-}C_6H_{13})_3SiCl$ [b]	4	98
9	$TeCl_4 + p\text{-}(Me_2HSi)_2C_6H_4$	1/1	$p\text{-}(Me_2ClSi)_2C_6H_4$ [c]	2	95

[a] Tellurium is the other product in all reactions. [b] ^1H NMR, alkyl δ 1.30 and 0.88 ppm, ν(Si–Cl) 513 cm^{-1}, b.p. 154–156 °C/5 mmHg [33]. [c] Recrystallised from ethanol/petroleum ether (30–60 °C); m.p. 88–90 °C, lit. [34] 87 °C. ^1H NMR, Ph δ 7.51 ppm (4 H); Me–Si δ 0.32 ppm (12 H)

soluble in benzene and other organic solvents even at low temperatures.

When the reactants in 1/2 mole ratio were refluxed for 6–10 h, diaryltellurium dichloride and chlorosilanes were formed (eq. 3).

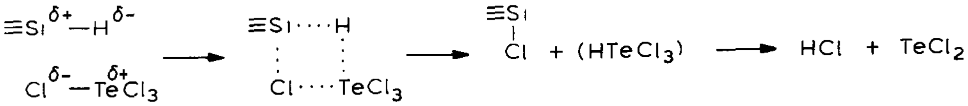
$$\mathrm{Ph_2SiH_2} + 2\,p\text{-}\mathrm{MeOC_6H_4TeCl_3} \xrightarrow[8\ \mathrm{h}]{\mathrm{reflux}}$$

$$\mathrm{Ph_2SiCl_2} + (p\text{-}\mathrm{MeOC_6H_4})_2\mathrm{TeCl_2} + \mathrm{Te} + 2\mathrm{HCl} \qquad (3)$$

The reactions were monitored by ^{1}H NMR spectroscopy. The evolution of HCl was confirmed by IR spectroscopy. The experimental details of these reactions are summarised in Table 2. Because all the tellurium and silicon products are known compounds, they were identified by mixed m.p. [1,18] or by comparing the IR spectra with the spectra of authentic samples. If the mixtures in the reactions described by eq. 2 were refluxed rather than stirred at room temperature, then some diaryltellurium dichloride was also obtained along with the ditelluride. Similarly, if the mixtures in the reactions described by eq. 3 were not refluxed for the appropriate time then some diaryl telluride was obtained.

In contrast to our observations with $TeCl_4$ and $RTeCl_3$, no appreciable reaction occurred between R_2TeCl_2 species (R = Ph, p-$MeOC_6H_4$) and organosilanes, as represented by $PhSiH_3$ and Ph_3SiH, even when the reactants were refluxed in benzene for 48 h in the presence of $AgNO_3$ which is known to enhance the elimination of HCl [2]. This was surprising because $RPhTeCl_2$ ($R = C_{12}H_{25}$, C_9H_{19}) are reduced to RPhTe by Ph_3SnH [19]. The R_2TeCl_2 compounds differ from $RTeCl_3$ and $TeCl_4$ in other properties. In the solid state, R_2TeCl_2 species show relatively small changes in Te–Cl bond lengths [14,20–23] whereas in $RTeCl_3$ compounds [20,24] and $TeCl_4$ [25] there is at least one distinctly longer and presumably weaker Te–Cl bond involved in bridging. Also, R_2TeCl_2 compounds tend not to form $[R_2TeCl]^+$ ions although $RTeCl_3$ species are known to form $[RTeCl_2]^+$ with counterions such as $[SbCl_6]^-$ [26] and $[MCl_6]^{2-}$, M = Sn, Ti [27].

The two distinct reactions involving organosilanes and $TeCl_4$ or $RTeCl_3$ suggest two reasonable mechanistic routes based on the assumption that the initial stage involves the classical [28] four-centre intermediate, e.g.



Tellurium(II) chloride is unstable in organic solvents [29] and can disproportionate to tellurium metal and $TeCl_4$ [30]. The latter would react again to eventually give tellurium metal as the only tellurium-containing product as we found experimentally (eq. 1).

A similar initial reaction involving $RTeCl_3$ would result in the formation of RTeCl species. The latter could combine to give R_2TeCl_2 and tellurium metal. Alternatively, further reaction of RTeCl with the silane would give the R_2Te_2 species and HCl that we found under milder conditions. It is known that ditellurides react with $RTeCl_3$ species to give R_2TeCl_2 and tellurium metal [31] so this could be the route, or at least an alternate route, to the dichlorides formed under more vigorous conditions.

TABLE 2

REACTIONS OF $RTeCl_3$ WITH ORGANOSILICON HYDRIDES IN BENZENE

No	Reactants (mole ratio)	Products	Temperature (°C)	Time (h)	Yield (%) silicon product
1	$PhSiH_3$ + p-$MeOC_6H_4TeCl_3$ (3/4)	$PhSiHCl_2$ + (p-$MeOC_6H_4)_2Te_2$	22	6	75
2	Ph_2SiH_2 + p-$MeOC_6H_4TeCl_3$ (1/2)	Ph_2SiCl_2 + (p-$MeOC_6H_4)_2TeCl_2$	Reflux	8	85
3	Ph_2SiH_2 + p-$MeOC_6H_4TeCl_3$ (3/4)	Ph_2SiCl_2 + (p-$MeOC_6H_4)_2Te_2$	22	6	83
4	Ph_2SiH_2 + $PhTeCl_3$ (3/4)	Ph_2SiCl_2 + Ph_2Te_2	22	8	75
5	Ph_2SiH_2 + p-$EtOC_6H_4TeCl_3$ (3/4)	Ph_2SiCl_2 + (p-$EtOC_6H_4)_2Te_2$	Reflux	4	80
6	Ph_3SiH + p-$EtOC_6H_4TeCl_3$ (1/1)	Ph_3SiCl + (p-$EtOC_6H_4)_2TeCl_2$	Reflux	10	75
7	Ph_2MeSiH + $PhTeCl_3$ (1/1)	$Ph_2MeSiCl$ + Ph_2TeCl_2	Reflux	7	95
8	(n-$C_6H_{13})_3SiH$ + p-$MeOC_6H_4TeCl_3$ (1/1)	(n-$C_6H_{13})_3SiCl$ + (p-$MeOC_6H_4)_2TeCl_2$	Reflux	6	90
9	Ph_2MeSiH + $PhTeCl_3$ (3/2)	$Ph_2MeSiCl$ + Ph_2Te_2	22	6	70
10	p-$(Me_2HSi)_2C_6H_4$ + p-$MeOC_6H_4TeCl_3$	p-$(Me_2SiCl)_2C_6H_4$ + (p-$MeOC_6H_4)_2TeCl_2$	22	8	95

Experimental

Organosilicon hydrides and $TeCl_4$ were purchased from Petrarch Systems Inc. and Alfa Products, respectively, and used without further purification. $RTeCl_3$ and R_2TeCl_2 were synthesised according to the methods already described [10,11,32]. All other reagents and solvents were purchased from commercial sources as reagent grade chemicals and purified by conventional methods.

^1H NMR spectra were recorded on a Varian EM-360 (60 MHz) spectrometer in $CDCl_3$ or CCl_4 solutions using tetramethylsilane as an external standard. IR spectra were recorded in Nujol mulls in CsI disks or in a gas cell on a Perkin–Elmer 180 spectrophotometer. All the reactions were carried out under moisture-free conditions. Because the experimental procedures were similar for all the reactions, only typical reactions are described below.

Reaction of diphenylsilane with tellurium tetrachloride

A solution of diphenylsilane (1.60 g, 8.66 mmol) in benzene (10 ml) was added dropwise to a stirred solution of tellurium tetrachloride (2.33 g, 8.66 mmol) in the same solvent (20 ml). The reaction mixture was stirred for 1/2 h and refluxed subsequently for 3 h until the ^1H NMR spectrum of the reaction mixture showed that the peak attributable to the Si–H protons had disappeared. Gas evolved was condensed in a liquid nitrogen trap and its IR spectrum recorded. After the mixture had been cooled to room temperature, the precipitated tellurium metal was filtered. On evaporation the filtrate gave diphenyldichlorosilane (2.08 g, yield 95%) b.p. 301–305 °C lit. [18] 302–305 °C.

Reaction of diphenylsilane with p-methoxyphenyltellurium trichloride

(i) At room temperature. Diphenylsilane (1.23 g, 6.68 mmol) and *p*-methoxyphenyltellurium trichloride (3.04 g, 8.91 mmol) were mixed in the same manner as described above. The reaction mixture was stirred for 6 h monitored by ^1H NMR spectroscopy, and filtered to remove any suspended impurities. The volume of the reaction mixture was reduced to 5 ml by evaporation in vacuum and the residue placed on a silica gel column (2 × 30 cm), which was developed with CCl_4. The first colourless fraction (100 ml) on evaporation yielded diphenyldichlorosilane (1.40 g, yield 83%), b.p. 301–304 °C, lit. [18] 302–305 °C, and the second red fraction (150 ml) gave bis(*p*-methoxyphenyl) ditelluride (1.18 g, yield 78%), m.p. 55–57 °C, lit. [10] 56–58 °C).

(ii) On refluxing. A similar reaction was set up with diphenylsilane (1.43 g, 7.75 mmol) and *p*-methoxyphenyltellurium trichloride (5.29 g, 15.5 mmol). The mixture was stirred for 1 h and subsequently refluxed for 8 h while monitoring by ^1H NMR spectroscopy. The mixture was then filtered quickly during cooling to remove tellurium metal. The filtrate on standing for a few hours gave a white precipitate which was filtered. Recrystallisation of the crude residue with CH_3CN gave pure $(p\text{-}MeOC_6H_4)_2TeCl_2$ (m.p. 183–184 °C, lit. [10] 181–182 °C), 2.75 g yield 85%). Diphenyldichlorosilane was recovered from the filtrate as described above.

Attempted reaction of phenylsilane with diphenyltellurium dichloride

To diphenyltellurium dichloride (1.50 g, 4.3 mmol) in benzene (20 ml), phenylsilane (0.15 g, 1.5 mmol) was added and the mixture was refluxed for 12 h.

Unreacted Ph_2TeCl_2 (90%) was recovered from the reaction mixture on cooling and filtration. The residue and the filtrate were transferred back to the reaction flask and 0.17 g (1 mmol) $AgNO_3$ was also added and refluxing resumed. After 48 h the reaction mixture was cooled and insoluble residue was filtered. The filtrate was concentrated to 5 ml and chromatographed on silica gel with benzene. The first colourless fraction (100 ml) contained unreacted $PhSiH_3$ and there was no sign of any other product even when the volume of eluent was one liter.

Similar reactions between $PhSiH_3/Ph_3SiH$ and (p-$MeOC_6H_4)_2TeCl_2$ also failed.

Acknowledgement

This work was supported in part by Operating Grants from the Natural Sciences and Engineering Research Council of Canada.

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