Cleavage of the Carbon–Silicon Bond in Alkynylsilanes by Platinum Compounds

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THE trimethylsilyl group has been used to protect the terminal ethynyl group in oxidative coupling[1] and hydrogenation[2] procedures. The overall procedure is dependent upon the ease of cleavage of the alkynyl carbon–silicon bond (C_{sp}–Si). Reagents which are reported to cause or induce this cleavage include alcoholic alkali,[1,3] aqueous alcoholic silver nitrate[2] and alcoholic potassium fluoride solutions.[4] One earlier reference noted that mercury(II) sulphate also assisted in the cleavage of the C_{sp}–Si bond.[5] During numerous attempts to prepare π-complexes of alkynylsilanes, we have noted a ready cleavage of the C_{sp}–Si bond by several Pt^{II} and Hg^{II} complexes. By comparison, several stable π-complexes of alkynylsilanes derived from iron and cobalt carbonyl[6] are known.

The addition of $PhC{\equiv}CSiMe_3$ to $Pt_2Cl_4(C_2H_4)_2$ in dry benzene at room temperature and under nitrogen yielded a deep red-brown reaction mixture and thence to a dark-brown precipitate containing platinum. Quantitative analysis of the solution by g.l.c. showed that for each mole of the dimeric platinum complex used, two moles of Me_3SiCl were generated within the time of mixing. The exact disposition of the ethylene is not known, but most probably it is simply displaced into the solvent. A very volatile component in the reaction mixture was noted by gas chromatography. We suggest that the gross reaction may be represented by reaction (1).

$$2PhC{\vdots}CSiMe_3 + Pt_2Cl_4(C_2H_4)_2 \rightarrow Me_3SiCl + 2C_2H_4 + PhC{\vdots}CPtCl \qquad (1)$$

Even when a large excess of the alkynylsilane was used, the amount of alkyne cleaved was determined by the quantity of $Pt_2Cl_4(C_2H_4)_2$ taken. The yield of Me_3SiCl could also be determined quantitatively by sweeping this product from the reaction mixture with a nitrogen-flow into a dilute base solution. In one instance the quantity of base neutralized in the hydrolysis of the chlorosilane was 96% of theoretical, based on reaction (1). In another reaction the total amount of chloride released upon the basic hydrolysis was determined gravimetrically as silver chloride and amounted to 100% of theoretical, after heating the reaction mixture for a few hours at 60°. An additional amount of chloride (< 10%) was detected only after continued heating at 60° for 4 days.

The exact nature of the platinum-containing residues is uncertain. However, it may be noted that all other alkynylsilanes studied (*e.g.* those in the Table), are likewise cleaved under these reaction conditions. In all cases the platinum-containing solids reveal ν ($C\vdots C$) bands in the range 2070—2110 cm.$^{-1}$

Catalytic cleavage of unsaturated groups from silicon by Zeise's salt in refluxing ethanol

Initial concentration at room temperature				
$KPtCl_3(C_2H_4)H_2O$	R in $RSiMe_3$		% Reaction[a]	Time (hr.)
$8\cdot7 \times 10^{-3}$M	$PhC\vdots C$	0·80	65	5
			100	10
8·7	$HC\vdots C$	0·80[b]	65	18
8·7	$Me_3SiC\vdots C$	0·75	63	20
8·7	$Bu^nC\vdots C$	0·55	63	47
			80	90
9·1	$Bu^tC\vdots C$	0·55	32	53
			50	75
8·7	$H_2C{:}CH$	0·77[b]	60	10
8·7	$CH_2{:}CHCH_2$	0·78	95	2·5
8·7	Ph	0·64	0	96
8·7	$PhCH_2$	0·78	0[c]	96

[a] % of silane lost and % of $Me_3Si\cdot OEt$ formed; [b] Reaction temperature, 40°; [c] Formation of a platinum mirror was observed in this reaction.

Cleavage of the C_{sp}–Si bond was also found to occur in refluxing absolute ethanol in the presence of a catalytic quantity of $Pt_2Cl_4(C_2H_4)_2$, or more conveniently $K[PtCl_3C_2H_4]H_2O$. The results of several reactions are given in the Table. In each instance, the number of moles of alkynylsilane consumed was equal to the moles of trimethylethoxysilane produced as determined quantitatively by g.l.c. The selected results indicate the relative ease with which the various alkynylsilanes, $RC\vdots C\cdot SiMe_3$, are cleaved: (R =)Ph > H > Me_3Si > Bu^n > Bu^t. Those reactions in which less than 100% reaction is reported could be carried to completion, and much more rapidly, by using larger quantities of catalyst.

The overall catalysed reaction of $PhC\vdots C\cdot SiMe_3$ with ethanol is shown in reaction (2). It should be noted that 1,1-diethoxy-1-phenylethane and not ethynylbenzene was obtained as a product. An independent catalytic reaction between ethanol and ethynylbenzene readily revealed that the rate

$$PhC\vdots C\cdot SiMe_3 + EtOH \xrightarrow{KPtCl_3C_2H_4} Me_3Si\cdot OEt + PhMeC(OEt)_2 \qquad (2)$$

of formation of 1,1-diethoxy-1-phenylethane exceeds the rate of cleavage of the C_{sp}–S bond under the reaction conditions represented by (2). Thus, ethynylbenzene formed in the cleavage step was readily converted to the ketal. Each product in reaction (2) was identified by b.p., i.r., and ^1H n.m.r.; a carbon–hydrogen analysis was also obtained for the ketal.

Zeise's salt (Table) also catalyses the cleavage of the vinyl and allyl groups from silicon in absolute ethanol. The organic products in these reactions, and for some of the acetylene reactions, have not been identified positively.

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