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ADDITION OF CARBON TETRACHLORIDE AND METHYL TRICHLOROACETATE TO SILICON-FUNCTIONAL VINYLSILANES

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Summary

Compounds of type $XCCl_2CH_2CHClSiY_3$ (X = Cl, COOMe; Y = Me, Cl, OEt) were obtained in good yields by the reactions of carbon tetrachloride and methyl trichloroacetate with vinylchlorosilanes or with vinylethoxysilanes in the presence of dichlorotris(triphenylphosphine)ruthenium(II).

Introduction

It has been known that organic polyhalides such as CBr_4, $CBrCl_3$, CF_3I, $CF_2ClCFClI$, $CF_2 = CFI$ and CF_3SO_2Cl add under free radical conditions to silicon-functional vinylsilanes (e.g., $CH_2 = CHSiCl_3$, $CH_2 = CHSiMeCl_2$, $CH_2 = CHSiMe_2Cl$, $CH_2 = CHSiPhCl_2$ and $CH_2 = CHSiMe(OEt)_2$) to give 1/1 adducts [1] and a useful tabular survey has been compiled by Seyferth [2]. However, the addition of less reactive polychloromethanes such as CCl_4 and $CHCl_3$ to vinylchlorosilanes or to vinylalkoxysilanes has not yet been explored, although such reactions of tetraorganosilanes bearing vinyl groups (e.g., $CH_2 = CHSiEt_3$, $CH_2 = CHSiPh_3$ and $(CH_2 = CH)_2SiMe_2$) have been reported [3]. As part of our studies on the addition reactions of polychloromethanes with olefins catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) [4], we have undertaken an investigation of the addition of carbon tetrachloride and methyl trichloroacetate to several silicon-functional vinylsilanes in the presence of the ruthenium(II) catalyst. This reaction provides a simple route to silicon-functional polychloroalkylsilanes of the type $XCCl_2CH_2CHClSiY_3$ (X = Cl, COOMe; Y = Me, Cl, OEt), which may be convenient precursors of various carbon-functional siloxanes [1e] or hydrosilanes [5].

Results and discussion

As a preliminary experiment, the benzoyl peroxide-catalyzed reaction of carbon tetrachloride with vinylmethyldichlorosilane or with vinyltriethoxysilane was conducted at reflux using a 1/2.5/0.03 mixture of the respective vinylsilane, carbon tetrachloride and the peroxide. GLC analysis of the resulting mixture, however, showed the formation of a complex mixture of the products which contained only small amounts (1—5%) of the expected 1/1 adducts.

We have previously showed that the dichlorotris(triphenylphosphine)-ruthenium(II) catalyzed addition of carbon tetrachloride and methyl trichloroacetate to simple olefins results in fairy clean reactions which give the expected 1/1 adducts in good yields [4,6]. We have found that silicon-functional vinylsilanes also react readily with these polychloromethanes in the presence of this ruthenium(II) catalyst. Thus, when a 1/2 mixture of vinylmethyldichlorosilane and carbon tetrachloride containing 0.4 mol% of the ruthenium(II) complex was refluxed for 17 h, 1,3,3,3-tetrachloropropylmethyldichlorosilane was produced in 67% isolated yield (eq. 1). Similarly, the reaction of vinyltriethoxysilane with carbon tetrachloride for 40 h in the presence of 0.4 mol% of the ruthenium(II) complex gave 1,3,3,3-tetrachloropropyltriethoxysilane in 52% isolated yield.

$$CCl_4 + CH_2 = CHSiMeCl_2 \xrightarrow{Ru^{II}} CCl_3CH_2CHClSiMeCl_2 \qquad (1)$$

Vinyldimethylchlorosilane, vinylmethyldiethoxysilane and vinyldimethylethoxysilane also reacted smoothly with carbon tetrachloride to give the corresponding 1/1 adducts in 51—68% isolated yields.

Methyl trichloroacetate also was found to react with vinylmethyldichlorosilane to give the expected 1/1 adduct in satisfactory yield (eq. 2)

$$CCl_3COOMe + CH_2 = CHSiMeCl_2 \xrightarrow{Ru^{II}} \underset{\text{(59\% isolated yield)}}{MeOOCCCl_2CH_2CHClSiMeCl_2} \qquad (2)$$

TABLE 1

REACTIONS OF CARBON TETRACHLORIDE OR METHYL TRICHLOROACETATE WITH SILICON-FUNCTIONAL VINYLSILANES IN THE PRESENCE OF DICHLOROTRIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(II) [a]

Vinylsilane (mmol)	Polychloromethane (mmol)	Product	Yield (%) [b]
$CH_2 = CHSiMeCl_2$ (810)	CCl_4 (2000)	$CCl_3CH_2CHClSiMeCl_2$	67 (93)
$CH_2 = CHSiMe_2Cl$ (100)	CCl_4 (200)	$CCl_3CH_2CHClSiMe_2Cl$	64 (100)
$CH_2 = CHSi(OEt)_3$ (720)	CCl_4 (1600)	$CCl_3CH_2CHClSi(OEt)_3$	50 (62)
$CH_2 = CHSiMe(OEt)_2$ (50)	CCl_4 (100)	$CCl_3CH_2CHClSiMe(OEt)_2$	51 (70)
$CH_2 = CHSiMe_2(OEt)$ (90)	CCl_4 (200)	$CCl_3CH_2CHClSiMe_2(OEt)$	68 (90)
$CH_2 = CHSiMeCl_2$ (50)	CCl_3COOMe (100)	$MeOOCCCl_2CH_2CHClSiMeCl_2$	59 (94)

[a] Reactions were carried out under reflux for 17—40 h under an atmosphere of nitrogen and concentrations of $RuCl_2(PPh_3)_3$ were 0.3—0.4 mol% based on the vinylsilane charged. [b] Isolated yields; those given in parentheses were determined by GLC.

TABLE 2

CHARACTERIZATION OF POLYCHLOROALKYLSILANES PREPARED

Compound	Bp (°C/mm Hg)	IR, principal absorptions (cm^{-1}) [a]	NMR, δ (ppm) [b]	Analysis (Found(calcd.) (%))	
				C	H
$CCl_3CH_2CHClSiMeCl_2$ ($C_4H_6Cl_6Si$)	99 (10)	1260 (Si—Me), 955, 835, 790, 690	1.00 (s, 3H, Si—Me), 3.13 (dd, 1H, $CCl_3C\mathit{H}H$, J = 8 and 15 Hz), 3.43 (dd, 1H, $CCl_3CH\mathit{H}$, J = 3 and 15 Hz), 3.84 (dd, 1H, CHCl, J = 3 and 8 Hz)	16.05 (16.29)	2.32 (2.05)
$CCl_3CH_2CHClSiMe_2Cl$ ($C_5H_9Cl_5Si$)	103 (10)	1255 (Si—Me), 955, 850, 790, 700, 690	0.54 (s, 3H, Si—Me), 0.63 (s, 3H, Si—Me), 3.02 (dd, 1H, $CCl_3C\mathit{H}H$, J = 8 and 15 Hz), 3.43 (dd, 1H, $CCl_3CH\mathit{H}$, J = 3 and 15 Hz), 3.75 (1H, CHCl, J = 3 and 8 Hz)	21.28 (21.88)	3.27 (3.31)
$CCl_3CH_2CHClSi(OEt)_3$ ($C_9H_{18}Cl_4O_3Si$)	163 (33)	1100 (Si—O—C), 955, 775, 700, 660	1.26 (t, 9H, $OCH_2C\mathit{H}_3$, J = 7 Hz), 3.05 (1H, $CCl_3C\mathit{H}H$, J = 8 and 15 Hz), 3.35 (dd, 1H, $CCl_3CH\mathit{H}$, J = 2 and 15 Hz), 3.59 (dd, 1H, CHCl, J = 2 and 8 Hz), 3.90 (quartet, 6H, OCH_2, J = 7 Hz)	31.65 (31.40)	5.18 (5.28)
$CCl_3CH_2CHClSiMe(OEt)_2$ ($C_8H_{16}Cl_4O_2Si$)	84 (2)	1260 (Si—Me), 1100 (Si—O—C), 790, 770, 700, 665	0.28 (s, 3H, Si—Me), 1.25(t, 6H, $OCH_2C\mathit{H}_3$, J = 7 Hz), 3.00 (dd, 1H, $CCl_3C\mathit{H}H$, J = 7 and 15 Hz), 3.35 (dd, 1H, $CCl_3CH\mathit{H}$, J = 2 and 15 Hz), 3.50 (dd, 1H, CHCl, J = 2 and 8 Hz), 3.85 (quartet, 4H, OCH_2, J = 7 Hz)	31.02 (30.59)	5.23 (5.13)
$CCl_3CH_2CHClSiMe_2(OEt)$ ($C_7H_{14}Cl_4OSi$)	128 (22)	1255 (Si—Me), 1100 (Si—O—C), 950, 780, 690	0.22 (s, 3H, Si—Me), 0.29 (s, 3H, Si—Me), 1.17 (t, 3H, $OC\mathit{H}_2CH_3$, J = 7 Hz), 3.05 (dd, 1H, $CCl_3C\mathit{H}H$, J = 8 and 15 Hz), 3.35 (dd, 1H, $CCl_3CH\mathit{H}$, J = 2 and 15 Hz), 3.55 (dd, 1H, CHCl, J = 2 and 8 Hz), 3.75 (quartet, 2H, OCH_2, J = 7 Hz)	29.45 (29.59)	4.94 (4.98)
$MeOOCCCl_2CH_2CHClSiMeCl_2$ ($C_6H_9Cl_5O_2Si$)	118 (7)	1755 (C = O), 1255 (Si—Me), 1170 (C—O—C), 805—790, 735, 690	0.95 (s, 3H, Si—Me), 3.03 (d, 2H, $CCl_2C\mathit{H}_2$, J = 6 Hz), 3.82 (s, 3H, OCH_3), 3.9 (1H, CHCl) [c]	22.54 (22.63)	2.93 (2.85)

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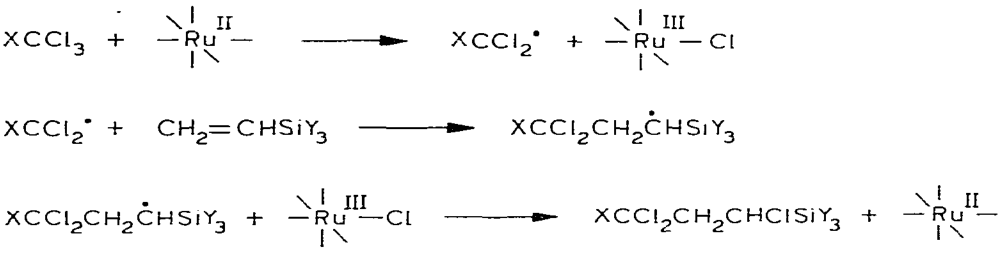
[a] All spectra were taken with neat samples. [b] All spectra were run in CCl_4 using Me_4Si as internal standard. [c] This proton was partially buried under the methyl ester signal at 3.82.

The results may be accounted for in terms of the following propagation steps by analogy with the previously proposed mechanism [4a,d,e] (Scheme 1).

Scheme 1



(X = Cl, COOMe, Y = Me, Cl, OEt)

Experimental

Boiling points are uncorrected. IR spectra were recorded on a Hitachi EPI-3G spectrophotometer. NMR spectra were taken on a Varian A-60D instrument. GLC analyses were carried out with an Ohkura Model 802T instrument, using 100 × 0.4 cm Teflon columns packed with 10% SE-30 and 10% Silicone KF-96 on Celite 545 (60/80).

Vinylmethyldichlorosilane, vinyldimethylchlorosilane, vinyltriethoxysilane, vinylmethyldiethoxysilane and vinyldimethylethoxysilane were supplied by the Toshiba Silicone Ltd. Reagent grade carbon tetrachloride and methyl trichloroacetate were purified by distillation prior to use. Dichlorotris(triphenylphosphine)ruthenium(II) was prepared according to literature directions [7]. Benzoyl peroxide was obtained commercially as a special grade and used without further purification.

General procedure for the addition reactions

All runs were conducted in essentially the same manner; therefore, only the reaction of carbon tetrachloride with vinylmethyldichlorosilane catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) is described in detail.

In a flask, equipped with a magnetic stirrer and a reflux condenser, was placed a mixture of 114 g (810 mmol) of the vinylsilane, 308 g (2000 mmol) of the chloride and 3.10 g (3.2 mmol) of the ruthenium(II) complex. The system was flushed with nitrogen and the solution was refluxed for 17 h with stirring. GLC analysis of the resulting mixture disclosed that the vinylsilane had been completely consumed and that the 1/1 adduct had been produced in 93% yield. The mixture then was diluted with 100 mL of petroleum ether and the precipitated catalyst was removed by filtration. Evaporation of low-boiling materials and subsequent distillation gave 160 g (67% yield) of 1,3,3,3-tetrachloropropylmethyldichlorosilane.

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