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The Reaction of Polyhalides with Allylsilanes Catalyzed by Copper(I) Chloride

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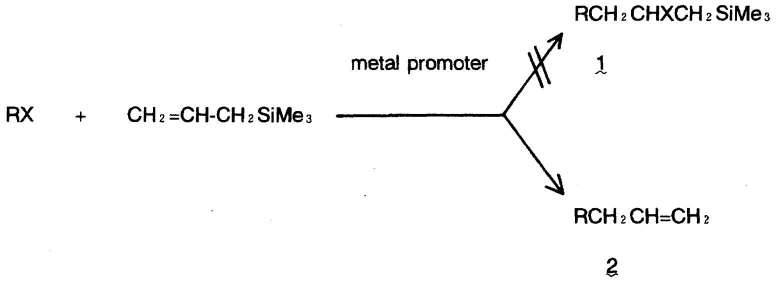
Allyltrimethylsilane reacted with polyhalogen compounds in the presence of copper species, such as copper(I) chloride, copper(II) chloride or metallic copper, to form polyhalo compounds containing an allyl group. Other allylsilane derivatives than allyltrimethylsilane were also subjected to a reaction with carbon tetrachloride. 3-Chloro- or 3-bromo-3-trimethylsilyl-1-propene gave 4,4,4-trichloro-1-trimethylsilyl-1-butene. Ethyl 1-trimethylsilylallyl carbonate afforded ethyl 4,4,4-trichloro-1-butenyl carbonate along with a hydrotrichloromethylation product. 2-Methyl-3-trimethylsilyl-1-propene yielded a product based on the addition of a trichloromethyl group followed by hydrogen-elimination from a 2-methyl group.

Allylsilanes have been extensively utilized as an interesting synthon undergoing a regiocontrolled attack with a variety of electrophiles, such as carbonyl compounds,[1] conjugated enones,[2] acyl halides,[3] acetals,[4] epoxides,[5] and alkyl halides[5,6] under promotion by Lewis acids to bring about a shift of the double bond along with an elimination of the silyl group. Extrusion of the silyl group from the carbocationic transition states or intermediates in these reactions is well accomplished owing to its electrofugal character, resulting in the generation of a migrated carbon–carbon double bond. The addition of polyhalides to allylsilanes, however, does not appear to have been heretofore performed, except for limited cases, such as in the radical-induced reaction of bromotrichloromethane with allyltrimethylsilane[7] or that of allyltris(trimethylsilyl)silane with organic halides, e.g., CCl_4, $BrCH_2COOEt$, or $BrCH_2CN$,[8] probably due to the difficulty to generate carbocationic intermediates under promotion by the Lewis acids. Metal salts or metals have been well known to promote the atom-transfer addition reaction of polyhalides to olefins.[9] Thus, at the start of this investigation, we imagined that polyhalogen compounds might add to allylsilanes under promotion by the metal species to afford 1 : 1 adducts, **1** holding the silyl group intact, which in turn would undergo dehalosilylation through action of a Lewis acid or a fluoride salt to result in the over-all formation of adducts bearing a migrated carbon–carbon double bond. Beyond such as initial scenario, we have found that a metal species, such as copper(I) chloride or copper metal, catalyzes the addition reaction of the polyhalogen compounds to the allylsilane accompanying desilylation to bring about the one-step formation of polyhalo compounds containing allyl group **2** (Scheme 1). It is noteworthy that the ene-polyhalides straightforwardly formed in our reaction using the allylsilane reveal a different regiochemistry from those afforded by the two-step procedure through a base-treatment of the 1 : 1 adducts of alkenes with polyhalogen compounds;[9c,9d] i.e., the former are the allyl type, while the latter are the vinyl type.

Results and Discussion

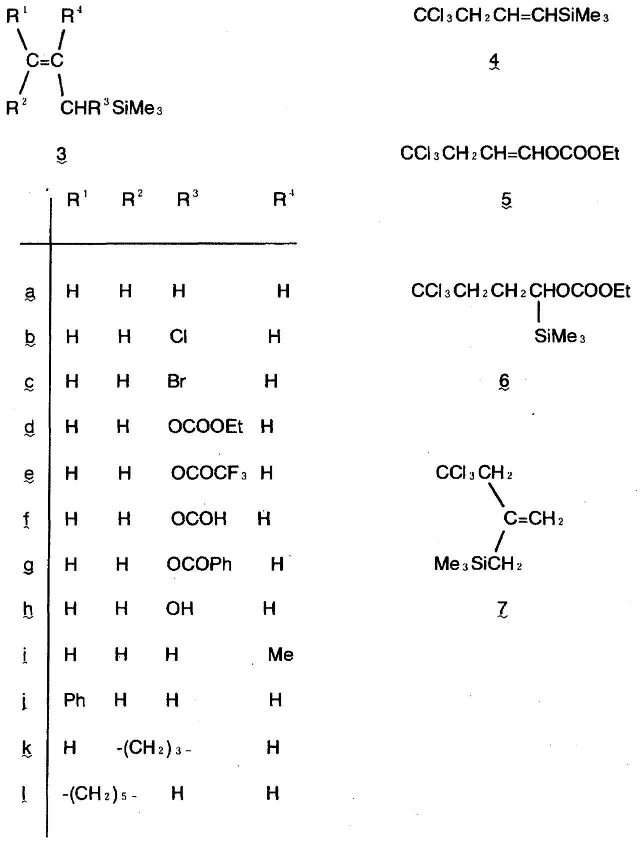
The reaction of carbon tetrachloride with allyltrimethylsilane **3a** was first tried under the same conditions as those used for the addition of polyhaloalkanes to 1-octene by Burton,[9c] i.e., refluxing of a solution containing copper(I) chloride (0.1 molar amount), 2-aminoethanol, and t-butyl alcohol under stirring for 24 h. As a result, 4,4,4-trichloro-1-butene (**2a**), which is not a 1 : 1 adduct, expected from the case using 1-octene, but formed through the addition reaction accompanying the desilylative double bond migration, was



Scheme 1.

obtained as a product. The yield of **2a**, however, was only modest (32%). Since the low yield of **2a** in the this reaction using an open vessel was supposed to be probably due to the high volarity of **3a**, the reaction was performed at 80 °C in a closed tube to afford an enhanced yield of **2a** (86%). Next, the effects of solvent, ligand, and metal species upon the yield of **2a** were explored in a thermal reaction in a closed tube. The yields of **2a**, however, were diminished by the use of other solvents than *t*-butyl alcohol (i.e., DMF, CH_3CN, DMSO, dioxane, 1-propanol, and benzene) or other ligands (i.e., Bu_3P and 2,2′-bpy[10]) instead of 2-aminoethanol. Subsequently, the influence of the metal promoters upon the formation of **2a** was investigated in the presence of 2-aminoethanol in *t*-butyl alcohol. An increase in an amount of copper(I) chloride (equimol. amount) rather diminished the yield of **2a** (13%). As with other metal salts than copper(I) chloride, copper(II) chloride[9g] brought about a comparable result with copper(I) chloride (**2a**; 85%), while iron(III) chloride[9g] afforded a far smaller yield of **2a** (9%). In a reaction using copper metal as a promoter in a closed tube, while an active one formed by the reduction of copper(I) chloride with lithium dihydronaphthylide[11] afforded a comparable result (86% yield) as in the case of using copper(I) chloride, a commercially available one proved to be less effective (42% yield). Those results concerning the reaction of carbon tetrachloride with **3a** under various conditions are listed in Table 1. For the cases where **2a** was afforded only in low yields (Table 1, Runs 3—12 and 14), other volatile products than **2a** were detected only as insignificant peaks by GC analysis of the reaction mixtures; thus, the major parts of **3a** can probably be assumed to be consumed for polymerization.

Next, the reaction of **3a** with a variety of polyhalogen compounds was performed in a closed tube in a solution consisting of copper(I) chloride, 2-aminoethanol, and *t*-butyl alcohol, which was the best of the examined conditions.



Scheme 2.

The results are given in Table 2. The reactivities of polyhaloalkanes to **3a** in our reaction are prone to be somewhat different from those in the reaction with 1-octene performed by Burton;[9c] i.e., polyhaloalkanes bearing a fluorine atom, such as CCl_3CF_3, $CClBrFCBrF_2$, or CCl_2FCClF_2, did not afford adducts **2** at all in spite of a complete consumption of **3a**, probably furnishing porimerization products, while

Table 1. Reaction of Carbon Tetrachloride with **3a**[a]

Run	Metal species	Ligand	Solvent	**3a** Conversion(%)[b]	**2a** Yield(%)[b,c]
1[d]	CuCl	$NH_2(CH_2)_2OH$	*t*-BuOH	25	32
2	CuCl	$NH_2(CH_2)_2OH$	*t*-BuOH	45	86
3	CuCl	$NH_2(CH_2)_2OH$	DMF	100	4
4	CuCl	$NH_2(CH_2)_2OH$	CH_3CN	100	17
5	CuCl	$NH_2(CH_2)_2OH$	DMSO	38	15
6	CuCl	$NH_2(CH_2)_2OH$	Dioxane	73	22
7	CuCl	$NH_2(CH_2)_2OH$	1-PrOH	90	29
8	CuCl	$NH_2(CH_2)_2OH$	Benzene	65	6
9	CuCl	Bu_3P	Benzene	69	7
10	CuCl	Bu_3P	*t*-BuOH	100	16
11	CuCl	2,2’-bpy	$Cl(CH_2)_2Cl$	70	0
12	CuCl[e]	$NH_2(CH_2)_2OH$	*t*-BuOH	100	13
13	$CuCl_2$	$NH_2(CH_2)_2OH$	*t*-BuOH	47	85
14	$FeCl_3$	$NH_2(CH_2)_2OH$	*t*-BuOH	100	9
15	Cu[f]	$NH_2(CH_2)_2OH$	*t*-BuOH	35	86
16	Cu[g]	$NH_2(CH_2)_2OH$	*t*-BuOH	20	42

a) Reaction conditions; T = 80 °C, *t* = 24 h, CCl_4 : **3a** : ligand : metal species = 4 : 2 : 1 : 0.2 mmol, solvent = 5 cm^3, apparatus = a closed tube.
b) Determined by GC analysis. c) Based on consumed **3a**. d) Reaction in an open vessel. e) Equimolar amount of CuCl was used.
f) Prepared by reduction of CuCl. g) Commercial source.

Table 2. Reaction of Polyhalogen Compounds with **3a** Catalyzed by CuCl in *t*-BuOH/2-Aminoethanol

Run	RX		Time	**3a** Conversion[a]	Product	**2** Yield[a,b]
	R	X	h	%		%
1	CCl_3	Cl	24	45	**2a**	86
2	CCl_3	Cl	50	100	**2a**	90(71)[c]
3[d]	CCl_3	Cl	24	20	**2a**	5
4[e]	CCl_3	Cl	24	21	**2a**	1
5	CCl_3	Br	24	100	**2a**	75
6	$CHBr_2$	Br	24	100	**2b**	56
7	CCl_2CCl_3	Cl	24	100	**2c**	73
8	CCl_2COCH_3	Cl	24	37	**2d**	71
9	CCl_2COCH_3	Cl	60	65	**2d**	70
10	CCl_2CN	Cl	24	100	**2e**	90(70)[c]
11	CCl_2COOEt	Cl	24	100	**2f**	49
12	CCl_2COCCl_3	Cl	24	70	**2g**	89
13	CBr_3	Br	24	50	**2h**	95

a) Determined by GC analysis. b) Based on consumed **3a**. c) Determined by preparative TLC isolation. d) Reaction in the presence of hydroquinone. e) Reaction in the presence of benzoquinone.

Table 3. Competitive Addition Reaction of CCl_4 to **3a** and Other Alkenes[a]

Run	Alkene (Conversion/%)[b]	Product	Yield (%)[b]
1	**3a** (12)	**2a**	10
	+	+	
	1-octene (100)	$CCl_3CH_2CHCl(CH_2)_5CH_3$	66
2	**3a** (7)	**2a**	4
	+	+	
	CH_2=CH–CN (56)	$CCl_3CH_2CHClCN$	34

a) Reaction conditions: $T = 80$ °C; $t = 24$ h; **3a** (2 mmol), alkene (2 mmol), CCl_4 (4 mmol), CuCl (0.2 mmol), 2-aminoethanol (1 mmol), and *t*-BuOH (5 cm^3) in a closed tube. b) Determined by GC analysis on the basis of the charged alkene.

Table 4. Reaction of Carbon Tetrachloride with Several Kinds of Allylsilanes **3**

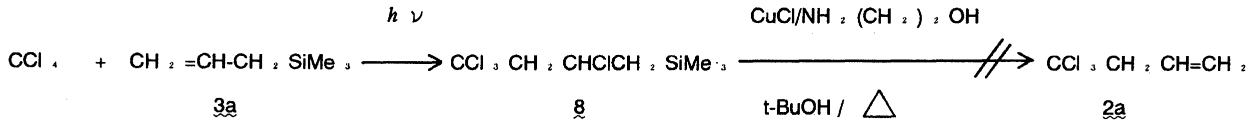
Run	**3**	**3** Conversion (%)	Product (Yield, %)[a]
1	**b**	100	**4** (42)
2	**c**	100	**4** (81)
3	**d**	100	**5** (70), **6** (19)
4	**i**	100	**7** (57)

a) Determined by GC analysis.

hexachloroethane formed **2c** in a good yield (73%). Next, the relative reactivities of **3a** and non-silylated olefins toward carbon tetrachloride were explored, revealing that the non-silylated olefin, whether it is unactivated or activated, such as 1-octene or acrylonitrile, brought about a better yield of the adduct compared with **3a**. These results, revealed in Table 3, are in sharp contrast with a stude by Hwu and his co-workers,[12] in which they found that the carboradical species generated via a treatment of the ketones with MnO_2 add more facilely to **3a** than 1-octene, giving the silicon-containing products.

Other allylsilane derivatives than **3a**, i.e., **3b**—**l**, were also subjected to a reaction with carbon tetrachloride. 1-Chloroallyltrimethylsilane (**3b**) did not form the 1,4,4,4-tetrachloro-1-butene anticipated from the result with **3a**, but yielded trimethyl-4,4,4-trichloro-1-butenylsilane (**4**), which was formally given via the elimination of a chlorine atom following the addition of a trichloromethyl group, in 42% yield as an only volatile product (Scheme 2). GC and ^{13}C NMR analyses of **4** revealed that it is composed of a single stereoisomer, although its accurate configuration has not yet been ascertained at this stage. The formation of **4** seems to be apparently curious, because the reaction of bromotrichloromethane with allyl chloride catalyzed by copper chloride has been reported to afford the 1 : 1 adduct without the elimination of a chlorine atom;[9d] furthermore, the reaction of carbon tetrachloride with allyl chloride in our system proved to furnish 1,1,1,3,4-pentachlorobutane, a product holding a chlorine atom intact. 1-Bromoallyltrimethylsilane (**3c**) also underwent a reaction accompanying the elimination of a bromine atom, resulting in the formation of **4** in a better yield (81%) than that from **3b**.

Next, allylsilanes bearing oxygen functionalities were used as substrates. Ethyl 1-trimethylsilylallyl carbonate (**3d**) afforded a silyl-eliminated product **5** in 70% yield along with a hydrogen-abstraction product **6** in 19% yield. Prod-



$$CCl_4 + \underset{\textbf{3a}}{CH_2{=}CH{-}CH_2SiMe_3} \xrightarrow{h\nu} \underset{\textbf{8}}{CCl_3CH_2CHClCH_2SiMe_3} \xrightarrow[t\text{-BuOH}\,/\,\Delta]{CuCl/NH_2(CH_2)_2OH} \!\!\!\!/\!/ \; \underset{\textbf{2a}}{CCl_3CH_2CH{=}CH_2}$$

Scheme 3.

uct **5** seems to be composed of a single stereoisomer based on GC and ^{13}C NMR analyses; its stereochemistry may be tentatively assigned to be a cis configuration from the coupling constant ($J = 7.7$ Hz) of olefinic protons in its ^{1}H NMR spectra. On the other hand, the allylsilanes bearing trifluoroacetoxy, a formyloxy group, or benzoyloxy in an α-position, i.e., **3e**—**g**, although perfectly consumed, seemed to afford no adduct, judging from the GC-MS of reaction mixtures containing volatile products in trace amounts from **3e**—**f** and the MS of the reaction mixture from **3g**, whose TLC analysis revealed the presence of complex components; also, the major parts of the substrates in these reactions might likely be used for polymerization. The allylsilane bearing a hydroxy substituent, **3h**, resulted in low consumption (40%) and no formation of an adduct, which was inferred from the GC-MS of the reaction mixture containing trace volatile products. Then, a reaction using trimethyl(2-methylallyl)silane (**3i**) as a branched allylsilane substrate was performed to bring about product **7**, derived via elimination of a hydrogen from the 2-methyl group with intact retainment of a silyl group in 57% yield as an only volatile product. Furthermore, allylsilane with the internal ene functionalities, **3j**—**l**, were examined. These substrates, however, were not consumed at all, probably due to steric reason. Those results using several kinds of allylsilanes are given in Table 4.

Concerning the reaction mechanism, the pathway in which a carboradical intermediate generated from a polyhalide via abstraction of a halogen atom by copper chloride is an active species for addition to the allylsilane might seem to be questionable, since the results of the reaction of the ketone-derived carboradical with the allylsilane reported by Hwu,[12)] i.e., the formation of a silyl-containing addition product, and the higher yield of the adduct with the allylsilane than that with 1-octene, differed from our results (Table 3). In the reaction of CCl_4 with **3a** in our reaction system, however, the addition of a radical scavenger (hydroquinone or benzoquinone) retarded the formation of **2a** (Table 2, Runs 3 and 4), and a reaction in the presence of a radical initiator (BPO) instead of CuCl and 2-aminoethanol yielded **2a**, although it was an insignificant component in a complex mixture. Furthermore, Sakurai and Hosomi have reported that the thermal reaction of a solution comprising bromotrichloromethane, **3a**, and BPO resulted in the formation of **2a**, where elimination of bromotrimethylsilane following the tentative formation of the 1 : 1 adduct was supposed as a possible pathway.[7)] Thus, it may be possibly assumed that the radical species operates as a reactive intermediate in our reaction, although the possibility of other active species than carboradical, such as a copper(III) intermediate through an oxidative addition of the polyhalide to copper(I) chloride,[13)] might not be entirely excluded. The mechanism, however, in which the 1 : 1 adduct **1** would be intermediately formed via the radical pathway, seems to be less possible for our reaction, since, when trimethyl(2,4,4,4-tetrachlorobutyl)silane (**8**), which was obtained as the 1 : 1 adduct through the photoreaction of carbon tetrachloride with **3a**, was submitted to a thermal reaction in a *t*-BuOH solution containing 2-aminoethanol and CuCl, **2a** was only little formed in spite of the consumption of **8** (Scheme 3). A report by Kosugi and Migita that, while allyltris(trimethylsilyl)silane, which should have a low Si–C bond energy, afforded allylation of organic halides in the radical reaction initiated by AIBN or $RuCl_2(PPh_3)_2$, allyltrimethylsilane gave no adduct with CCl_4 in an AIBN-initiated reaction[8)] also seems to make the operation of the simple radical pathway in our reaction suspicious. Although the working scenario for the formation of **2** is not clearly confirmed at this stage, a pathway which contains the addition of the polyhalide-derived radical species to the allylsilane followed by oxidation with copper(II) halide, effecting the elimination of the silyl cation, may be postulated as a possible candidate.

Experimental

Instrument. IR spectra were recorded in cm^{-1} using a Horiba FT-210 spectrometer. ^{1}H (60 MHz) and ^{13}C (15 MHz) NMR spectra were recorded with a JEOL FX60 spectrometer for $CDCl_3/CCl_4$ solutions using Me_4Si as internal standard although ^{13}C spectra of quaternary carbons could not be detected, due to the low-resolution ability of this instrument. Mass spectra were obtained at 70 eV using a Hitachi M-80B instrument. GC was performed with a Shimadzu GC-6A instrument.

Materials. THF and diethyl ether were purified by distillation after drying over Na and then $LiAlH_4$. Active-copper metal was prepared by the reduction of copper(I) chloride with lithium dihydronaphthylide according to a method by Rieke.[11)] Compounds **3b**—**g** were prepared by the lithium dicyclohexylamine-treated reaction of corresponding allyl halides and allyl esters with chlorotrimethylsilane according to a method by Hosomi.[14)] Compound **3h** was afforded by the reaction of allyl alcohol with chlorotrimethylsilane in the presence of *n*-BuLi and *t*-BuLi according to a method by Danheiser.[15)] Compounds **3i**—**k** were given by reactions of chlorotrimethylsilane with crotyl chloride, cinnamyl chloride, and 3-bromocycloxehene, respectively, under promotion with magnesium.[16,17)] Compound **3l** was yielded by a Wittig reaction of (2-silylethylidene)triphenylphosphorane with cyclohexanone according to a method by Fleming and Paterson.[5)]

Reaction of a Polyhalide with an Allylsilane. A solution or suspension comprising an allylsilane (2 mmol), a polyhalogen compound (4 mmol), 2-aminoethanol (0.061 g, 1 mmol), a metal species (0.2 mmol), and *t*-butyl alcohol (5 cm^3) was stirred in a closed tube at 80 °C for 24 h or longer. Then, the reaction mixture was poured into water (80 cm^3), extracted with diethyl ether (30 cm^3 × 2) and dried over $MgSO_4$. After the solvent was evaporated, the product was purified by preparative GC or TLC.

4,4,4-Trichloro-1-butene (2a): A colorless oil; IR (neat) 3087, 1645, 930, 800, 714 cm^{-1}; ^{1}H NMR $\delta = 6.25$—5.02 (3H, m, C(2)-H–C(1)H), 3.44 (2H, d, $J = 6.9$ Hz, C(3)H); ^{13}C NMR $\delta = 130.1$, 121.7, 58.7; MS (EI) *m*/*z* 160 [(M+2)$^+$; 14%], 158 (M$^+$; 15), 125 (68), 123 (98), 111 (100), 109 (98), 98 (83), 96 (98), 87 (93), 51 (89). HRMS Found: *m*/*z* 157.9439. Calcd for $C_4H_5Cl_3$: M, 157.9456.

4,4-Dibromo-1-butene (2b): A colorless oil; IR (neat) 3084, 1639, 940, 808, 733 cm^{-1}; ^{1}H NMR $\delta = 6.10$—4.96 (3H, m, C(2)H–C(1)H), 5.01 (1H, t, $J = 6.9$ Hz, C(4)H), 3.00 (2H, t, $J = 6.9$ Hz, C(3)H); ^{13}C NMR $\delta = 132.8$, 119.7, 49.0, 43.4; MS (EI) *m*/*z* 214 [(M+2)$^+$; 0.4%], 212 (M$^+$; 0.2), 135 (72), 133 (76), 53 (100). HRMS Found: *m*/*z* 132.9676. Calcd for C_4H_6Br: M − Br, 132.9653.

4,4,5,5,5-Pentachloro-1-penten (2c): A colorless oil; IR (neat) 3084, 1645, 928, 781, 729 cm^{-1}; ^{1}H NMR $\delta = 6.20$—4.98 (3H, m, C(2)H–C(1)H), 3.14 (2H, d, $J = 6.9$ Hz, C(3)H); ^{13}C NMR $\delta = 130.3$, 121.2, 46.1; MS (EI) *m*/*z* 242 [(M+2)$^+$; 2.9%], 240 (M$^+$; 1.6), 168 (60), 166 (95), 164 (71), 145 (73), 143 (71), 125 (57), 123 (70), 87 (71), 41 (100). HRMS Found: *m*/*z* 239.8816. Calcd for $C_5H_5Cl_5$: M, 239.8833.

3,3-Dichloro-5-hexen-2-one (2d): A colorless oil; IR (neat) 3085, 1736, 1645, 928, 802, 710 cm^{-1}; ^{1}H NMR $\delta = 6.15$—4.94 (3H, m, C(6)H–C(5)H), 3.07 (2H, d, $J = 6.9$ Hz, C(4)H), 2.32 (3H, s, C(1)H); ^{13}C NMR $\delta = 130.4$, 120.9, 46.5, 23.0; MS (EI) *m*/*z* 168 [(M+2)$^+$; 0.3%), 166 (M$^+$; 0.4), 133 (3), 131 (11), 87 (10), 43 (100). HRMS Found: *m*/*z* 165.9957. Calcd for $C_6H_8OCl_2$: M, 165.9952.

2,2-Dichloro-4-pentenenitrile (2e): A colorless oil; IR (neat) 3089, 2247, 1645, 929, 800, 714 cm^{-1}; ^{1}H NMR $\delta = 6.01$—5.08 (3H, m, C(5)H–C(4)H), 3.01 (2H, d, $J = 6.9$ Hz, C(3)H); ^{13}C NMR $\delta = 127.9$, 123.5, 51.8; MS (EI) *m*/*z* 151 [(M+2)$^+$; 2%], 149 (M$^+$; 3), 116 (41), 114 (100), 78 (78), 62 (98), 41 (98). HRMS Found: *m*/*z* 114.0136. Calcd for C_5H_5NCl: M − Cl, 114.0110.

Ethyl 2,2-Dichloro-4-pentenoate (2f): A colorless oil; IR (neat) 3088, 1765, 1248, 1092, 933, 829, 683 cm^{-1}; ^{1}H NMR $\delta = 6.10$—4.94 (3H, m, C(5)H–C(4)H), 4.20 (2H, q, $J = 6.9$ Hz, CH_2O), 3.00 (2H, d, $J = 6.9$ Hz, C(3)H), 1.41 (3H, t, $J = 6.9$ Hz, CH_3); ^{13}C NMR $\delta = 130.1$, 121.1, 63.3, 49.1, 13.8; MS (EI) *m*/*z* 198 [(M+2)$^+$; 0.6%], 196 (M$^+$; 1), 163 (22), 161 (55), 125 (60), 123 (100), 87 (89). HRMS Found: *m*/*z* 196.0060. Calcd for $C_7H_{10}O_2Cl_2$: M, 196.0057.

1,1,1,3,3-Pentachloro-5-hexen-2-one (2g): A colorless oil; IR (neat) 3088, 1749, 1645, 933, 816, 650 cm^{-1}; ^{1}H NMR $\delta =$ 6.08—5.00 (3H, m, C(5)–C(6)H), 3.13 (2H, d, $J = 6.9$ Hz, C(4)-H); ^{13}C NMR $\delta = 130.1$, 123.3, 51.3; MS (EI) *m*/*z* 270 [(M+2)$^+$; 6%], 268 (M$^+$; 4), 234 (39), 232 (27), 198 (22), 196 (14), 170 (50), 168 (49), 123 (100). HRMS Found: *m*/*z* 267.8754. Calcd for $C_6H_5OCl_5$: M, 267.8782.

4,4,4-Tribromo-1-butene (2h): A colorless oil; IR (neat) 3084, 1639, 939, 629 cm^{-1}; ^{1}H NMR $\delta = 6.12$—5.02 (3H, m, C(2)–C-(1)H), 3.60 (2H, d, $J = 6.9$ Hz, C(3)H); ^{13}C NMR $\delta = 132.7$, 121.1, 63.0; MS (EI) *m*/*z* 292 [(M+2)$^+$; 0.6%], 290 (M$^+$; 0.2), 215 (83), 213 (100), 211 (85), 133 (69), 131 (69), 107 (43), 105 (44), 81 (52), 79 (52). HRMS Found: *m*/*z* 289.7963. Calcd for $C_4H_5Br_3$: M, 289.7943.

4,4,4-Trichloro-1-butenyl)trimethylsilane (4): A colorless oil; IR (neat) 3081, 1624, 862, 839 cm^{-1}; ^{1}H NMR $\delta = 5.97$ (2H, quasi br.s, C(2)H–C(1)H), 3.23 (2H, d, $J = 5.1$ Hz, C(3)H), 0.10 (9H, s, $SiCH_3$); ^{13}C NMR $\delta = 140.4$, 138.4, 62.7, 1.5; MS (EI) *m*/*z* 232 [(M+2)$^+$; 0.1%], 230 (M$^+$; 0.1), 217 (9), 215 (9), 181 (9), 179 (9), 113 (79), 95 (90), 93 (100), 73 (91). HRMS Found: *m*/*z* 214.9622. Calcd for $C_6H_{10}Cl_3Si$: M − CH_3, 214.9616.

Ethyl 4,4,4-trichloro-1-butenyl Carbonate (5): A colorless oil; ^{1}H NMR $\delta = 7.16$ (1H, d, $J = 7.7$ Hz, C(1)H), 5.30 (1H, q, $J = 7.7$ Hz, C(2)H), 4.13 (2H, q, $J = 6.9$ Hz, $O\underline{CH_2}CH_3$), 3.37 (2H, d, $J = 7.7$ Hz, C(3)H), 1.40 (3H, t, $J = 6.9$ Hz, CH_3); ^{13}C NMR $\delta = 139.1$, 105.0, 64.4, 49.9, 14.0; MS (CI) *m*/*z* 249 [(M+2+H)$^+$; 45%], 247 [(M+H)$^+$; 45]; MS (EI) *m*/*z* 176 (5%), 174 (5), 105 (6), 103 (20), 85 (26), 75 (32), 73 (77), 57 (100). HRMS Found: *m*/*z* 173.9429. Calcd for $C_4H_5OCl_3$: M − $CH_2{=}CH_2$ − CO_2, 173.9408.

Ethyl 4,4,4-Trichloro-1-trimethylsilylbutyl Carbonate (6): A colorless oil; ^{1}H NMR $\delta = 4.20$ (1H, t, $J = 6.9$ Hz, $\underline{CH}SiMe_3$), 4.09 (2H, q, $J = 6.9$ Hz, $O\underline{CH_2}CH_3$), 3.05 (2H, t, $J = 6.9$ Hz, CCl_3CH_2), 2.67—2.25 (2H, m, $CCl_3CH_2\underline{CH_2}$), 1.38 (3H, t, $J = 6.9$ Hz, $OCH_2\underline{CH_3}$), 0.08 (9H, s, $SiCH_3$); ^{13}C NMR $\delta = 71.8$, 66.6, 62.3, 51.4, 16.6, 1.4; MS (CI) *m*/*z* 323 [(M+2+H)$^+$; 3%], 321 [(M+H)$^+$; 3]; MS (EI) *m*/*z* 287 (6%), 285 (8), 93 (64), 73 (100). HRMS Found: *m*/*z* 285.0467. Calcd for $C_{10}H_{19}O_3Cl_2Si$: M − Cl, 285.0482.

Trimethyl[2-(2,2,2-trichloroethyl)allyl]silane (7): A colorless oil; IR (neat) 3084, 1633, 851, 776, 712 cm^{-1}; ^{1}H NMR $\delta = 4.90$ (2H, br.s, $C{=}CH_2$), 3.13 (2H, s, CCl_3CH_2), 1.89 (2H, s, CH_2TMS), 0.03 (9H, s, $SiCH_3$); ^{13}C NMR $\delta = 117.9$, 62.7, 29.0, 1.5; MS (EI) *m*/*z* 246 [(M+2)$^+$; 0.4%], 244 (M$^+$; 0.4), 138 (38), 136 (60), 103 (44), 101 (78), 95 (53), 93 (93), 73 (100). HRMS Found: *m*/*z* 243.9994. Calcd for $C_8H_{15}SiCl_3$: M, 244.0007.

Trimethyl(2,4,4,4-tetrachlorobutyl)silane (8): A colorless oil; ^{1}H NMR $\delta = 4.64$—4.14 (1H, m, C(2)H), 3.15 (2H, quasi t, $J = 5.2$ Hz, C(3)H), 1.43 (2H, quasi d, $J = 8.6$ Hz, C(1)H), 0.08 (9H, s, $SiCH_3$); ^{13}C NMR $\delta = 69.5$, 56.2, 30.2, 0.8; MS (CI) *m*/*z* 269 [(M+2+H)$^+$; 13%], 267 [(M+H)$^+$; 9]; MS (EI) *m*/*z* 160 (12%), 158 (12), 125 (98), 123 (98), 111 (99), 109 (99), 98 (99), 96 (99), 73 (96), 51 (100).

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