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# Addition Reactions of Polyhalides to Ketene Silyl Acetals and Silyl Enol Ethers under Thermal or Photo-Irradiated Conditions without a Promoter

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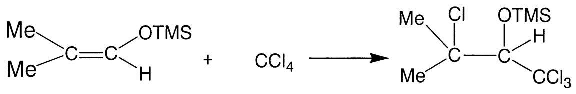
The reactions of ketene silyl acetals and silyl enol ethers in a $CCl_4$ solution containing no promoter under ambient temperature, reflux, or photo-irradiation conditions afforded products via the addition of a trichloromethyl group to those silyl substrates. Polyhalides other than $CCl_4$ were subjected to photoreactions in a hexane solution, resulting in the formation of carbonyl derivatives based on the addition of polyhalogenated alkyl groups.

The reactions[1] of ketene silyl acetals or silyl enol ethers with a variety of carbon nucleophiles, including carbonyl compounds, conjugated enones, or organic halides, in the presence of a Lewis acid or a desilylative reagent, such as a fluoride compound, are known to give $\alpha$-functionalized carbonyl compounds. As with organic halides, while monohalogen compounds, such as tertiary, benzyl, and allyl compounds, afford alkylated products in the presence of a Lewis acid, e.g., titanium(IV) chloride,[2] zinc(II) chloride,[3] or silver(I) perchlorate,[4] polyhalides, such as carbon tetrachloride, give $\beta$-halo-$\alpha,\beta$-unsaturated carbonyl derivatives in the reaction catalyzed with copper(I) chloride,[5] triethylborane,[6] or a Ru(II) complex.[7] These reactions of polyhalides are assumed to proceed via the abstraction of a halogen atom by a metal promoter to generate polyhaloalkyl radicals. In a preliminary communication,[8] we presented that ketene silyl acetals and silyl enol ethers can be reacted in a $CCl_4$ solution containing no metal promoter at ambient or reflux temperature, or under photo-irradiation, to afford products based on the addition of a trichloromethyl group to silyl substrates. In this paper, we wish to report on the details of reactions of silyl substrates in a $CCl_4$ solution and an extension to a reaction with polyhalides other than $CCl_4$ in a hexane solution under photo-irradiation.

## Results

**Reaction of Ketene Silyl Acetals and Aldehyde-Derived Silyl Enol Ethers in a $CCl_4$ Solution.** A $CCl_4$ solution of ketene silyl acetal **1a** from *N*,*N*-dimethylglycine methyl ester was stirred at ambient temperature for 3 h; a VPC analysis of the resulting mixture revealed the consumption of **1a** and the appearance of one product. The product was found to be *N*,*N*-dimethyl-2-trichloromethylglycine methyl ester **2a** based on spectral data after isolation; its yield was 57%. Raising or lowering the reaction temperature resulted in a decrease in the yield of **2a** (18% and 27% at 76 °C and 0 °C, respectively). The ketene silyl acetal **1b** from methyl methoxyacetate in a $CCl_4$ solution furnished the 2-trichloromethyl ester **2b** in an 81% yield under reflux conditions, although no reaction occurred at ambient temperature. The ketene silyl acetal **1c** from methyl propionate, which possesses no strongly electron-donating substituent, such as an amino or alkoxy group, afforded the 2-trichloromethyl ester **2c** in a good yield (81%) by the reaction under photo-irradiation conditions, while **2c** was obtained in low yield (29%) under reflux conditions. The ketene silyl acetals **1d–g** from the linear or branched aliphatic esters also gave $\alpha$-trichloromethylation products **2d–g** under photo-irradiation conditions. In the case of **1b**, however, a photoreaction diminished the yield of **2b** compared with that obtained from a thermal reaction. These results are given in Table 1.

In turn, aldehyde-derived silyl enol ethers were subjected to photoreactions in a $CCl_4$ solution. As shown in Table 2, **3a–c** produed aldehydes **4a–c** bearing $\alpha$-trichloromethyl substituents in good yields. On the other hand, as shown in Scheme 1, the silyl enol ether **5** derived from a branched aldehyde afforded the 1:1 adduct **6** based on the addition of a trichloromethyl group to the carbon bearing a trimethylsilyl group.

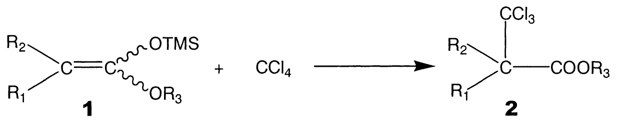


**5** **6** 35%

Scheme 1.

**Effects of Solvent.** The reaction of ketene silyl acetals **1a** and silyl enol ether **3b** with $CCl_4$ was performed in the presence of a solvent; the results are given in Table 3. THF proved to be the best of the examined solvents for the reactions of **1a** at ambient temperature (Table 3, run 6), although the yield of product **2a** was rather low compared to that in a $CCl_4$ solution (cf. Table 1, run 1). On the other hand, in the photoreaction of **3b**, the yield of the adduct **4b** in a hexane solution was better than those in polar solvents, such as acetone, acetonitrile, THF, or diethyl ether (Table 3, runs 8–12), and comparable with that

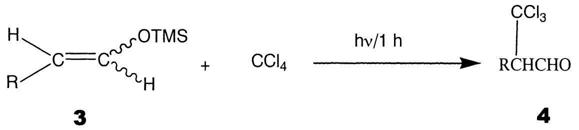
Table 1. Reaction of Ketene Silyl Acetals in a $CCl_4$ Solution



| Run | Substrate | | | | | Conditions | Product | Yield[a]/% |
|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | *E*/*Z* | | | | |
| 1 | $Me_2N$ | H | Me | 50/50 | **1a** | 3 h/rt | **2a** | 57 |
| 2 | | | | | | 3 h/76 °C | | 18 |
| 3 | | | | | | 20 h/0 °C | | 27 |
| 4 | MeO | H | Me | 0/100 | **1b** | 3 h/76 °C | **2b** | 81 |
| 5 | | | | | | 4 h/rt | | 0 |
| 6 | | | | | | 3 h/*hν* | | 65 |
| 7 | Me | H | Me | 75/25 | **1c** | 3 h/76 °C | **2c** | 29 |
| 8 | | | | | | 1 h/*hν* | | 81 |
| 9 | Et | H | Et | 74/26 | **1d** | 1 h/*hν* | **2d** | 73 |
| 10 | Bu | H | Et | 60/40 | **1e** | 4 h/*hν* | **2e** | 62 |
| 11 | Me | Me | Me | | **1f** | 1 h/*hν* | **2f** | 50 |
| 12 | $Bu^t$ | H | Et | 68/32 | **1g** | 1 h/*hν* | **2g** | 18 |

a) Determined by VPC.

Table 2. Reaction of Aldehyde-Derived Silyl Enol Ethers in a $CCl_4$ Solution



| Run | Substrate | | | Product | Yield[a]/% |
|---|---|---|---|---|---|
| | R | *E*/*Z* | | | |
| 1 | Et | 39/61 | **3a** | **4a** | 85 |
| 2 | pentyl | 40/60 | **3b** | **4b** | 79(65)[b] |
| 3 | hexyl | 42/58 | **3c** | **4c** | 68 |

a) Determined by VPC. b) Based on TLC isolation.

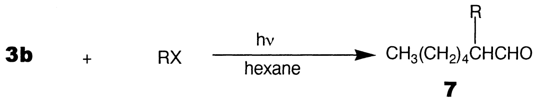
Table 3. Reaction of Silyl Substrates with $CCl_4$ in the Presence of a Solvent[a]

| Run | Substrate | Solvent | Conditions | Product | Yield[b] /% |
|---|---|---|---|---|---|
| 1 | **1a** | Hexane | 4 h/rt | **2a** | 2 |
| 2 | **1a** | acetone | 4 h/rt | **2a** | 6 |
| 3 | **1a** | $CH_2Cl_2$ | 4 h/rt | **2a** | 7 |
| 4 | **1a** | $CH_3CN$ | 4 h/rt | **2a** | 20 |
| 5 | **1a** | $Et_2O$ | 4 h/rt | **2a** | 23 |
| 6 | **1a** | THF | 4 h/rt | **2a** | 34 |
| 7 | **3a** | Hexane | 1 h/*hν* | **4a** | 80 |
| 8 | **3b** | Hexane | 1 h/*hν* | **4b** | 77 |
| 9 | **3b** | $Et_2O$ | 1 h/*hν* | **4b** | 69 |
| 10 | **3b** | THF | 1 h/*hν* | **4b** | 68 |
| 11 | **3b** | $CH_3CN$ | 1 h/*hν* | **4b** | 50 |
| 12 | **3b** | Acetone | 1 h/*hν* | **4b** | 32 |

a) Silyl substrate (2 mmol), $CCl_4$ (4 mmol), and solvent (5 mL). b) Determined by VPC.

in a $CCl_4$ solution (cf. Table 2, run 2). The photoreaction of the aldehyde-derived silyl enol ether **3a** with $CCl_4$ in a hexane solution also gave **4a** in a good yield (Table 3, run 7).

Table 4. Photoreaction of **3b** with Polyhalides in a Hexane Solution

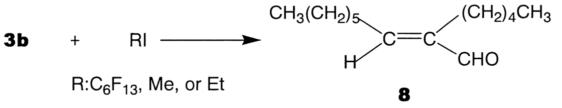


| Run | RX | | Time/h | Product | Yield /% |
|---|---|---|---|---|---|
| | R | X | | | |
| 1 | $CCl_2CCl_3$ | Cl | 24 | **7a** | 66[a] |
| 2 | $CCl_2CF_3$ | Cl | 24 | **7b** | 61[b] |
| 3 | $CClFCClF_2$ | Cl | 24 | **7c** | 48[a] |
| 4 | $CClFCBrF_2$ | Br | 1 | **7d** | 42[a] |

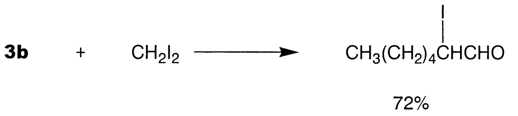
a) Based on TLC isolation. b) Determined by VPC.

**Photoreaction of Aldehyde-Derived Silyl Enol Ethers in a Hexane Solution.** Photoreactions of the aldehyde-derived silyl enol ethers with polyhalides other than $CCl_4$ were performed in a hexane solution. At first, **3b** was used as a silyl enol ether substrate. Hexachloroethane formed product **7a** based on the addition of a $CCl_2CCl_3$ group (Table 4, run 1). 1,1,1-Trichloro-2,2,2-trifluoroethane and 1,1,2-trichloro-1,2,2-trifluoroethane afforded products **7b** and **7c**, respectively, by the addition of dechlorinated polyhaloalkyl groups (Table 4, runs 2 and 3). The structure of **7c** was assigned by detection of the ion based on fragmentation of the $CClF_2$, not the $CCl_2F$, group in its mass spectra. 1-Chloro-1,2-dibromo-1,2,2-trifluoroethane gave product **7d** based on the addition of a $CClFCBrF_2$ group to **3b** (Table 4, run 4), the structure of which was inferred by finding that **7d** was transformed to a dehydrochlorinated compound through treatment with a base ($Na_2CO_3$).

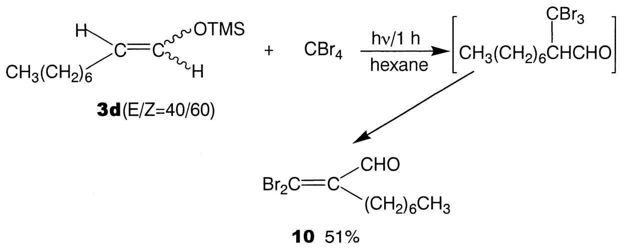
The reaction using 1-iodoperfluorohexane as a polyhalide did not form a product based on the addition of the perfluorohexyl group, but gave product **8** which is based on an aldol-condensation reaction of **3b**. The use of other monoiodine-



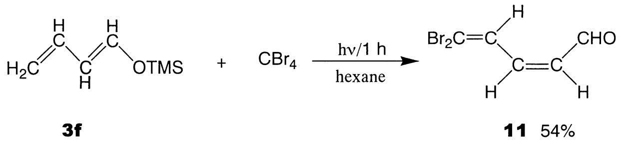
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

containing compounds, such as methyl or ethyl iodide, also gave **8** as a product (Scheme 2), whereas diiodomethane afforded 2-iodoheptanal (Scheme 3).

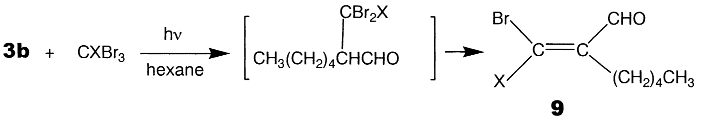
The products obtained by reactions with $CBr_4$ and $CHBr_3$ were the compounds **9a** and **9b**, respectively, based on the addition of the tri- and dibromomethyl groups to **3b**, followed by dehydrobromination (Table 5).

Next, aldehyde-derived silyl enol ethers other than **3b** were subjected to photoreactions with $CBr_4$ in a hexane solution. As shown in Scheme 4, **3d** furnished product **10**, which is consistent with the formation of **9a** from **3b**. 1-Trimethylsilyloxy-1,3-butadiene **3f** gave product **11** based on the consecutive events involving the addition of a tribromomethyl group onto terminal $sp^2$ carbon,[9] the migration of a carbon–carbon double bond, desilylation, and dehydrobromination (Scheme 5).

**Photoreaction of Ketone-Derived Silyl Enol Ethers.** Subsequently, the ketone-derived silyl enol ethers were subjected to photoreactions in a $CCl_4$ solution and in a hexane solution containing a polyhalide. The reactions of 3-trimethylsiloxy-2-pentene **12a** and 4-trimethylsiloxy-3-heptene **12b** in a $CCl_4$ solution gave products **13a** and **13b** via the addition of a trichloromethyl group, followed by migration of the carbon-carbon double bond with a retention of the silyl group; the reactions of **12a**, **12c**, and **12d** with $CCl_4$ in a hexane solution also gave products of silyl enol-type **13a**, **13c**, and **13d** (Table 6).

On the other hand, 3,3-dimethyl-2-trimethylsiloxy-1-butene **14** derived from a ketone possessing no $\alpha'$-hydrogen gave, by the reaction in a $CCl_4$ solution, the $\beta,\beta$-dichloro-$\alpha,\beta$-unsaturated ketone **15** based on the addition of a trichloromethyl

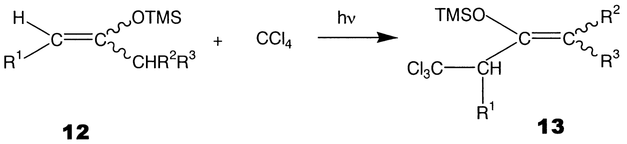
Table 5. Photoreaction of **3b** with $CBr_4$ or $CHBr_3$ in a Hexane Solution



| Run | X | Time/h | Product | Yield /% |
|---|---|---|---|---|
| 1 | Br | 1 | **9a** | 72[a)] |
| 2 | H | 3 | **9b** | 70[b)] |

a) Based on TLC isolation. b) Determined by VPC.

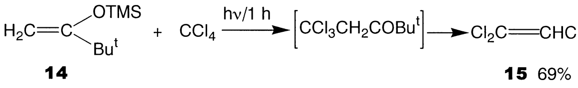
Table 6. Reaction of Ketone-Derived Silyl Enol Ethers with $CCl_4$



| Run | Substrate | | | | | Solvent | Time/h | Product | | Yield[a)]/% |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | *E/Z* | | | | *E/Z* | | |
| 1 | Me | Me | H | 45/55 | **12a** | $CCl_4$ | 1 | 50/50 | **13a** | 67 |
| 2 | Et | Et | H | 42/58 | **12b** | $CCl_4$ | 2 | 50/50 | **13b** | 61 |
| 3 | | | | | **12a** | hexane | 6 | 50/50 | **13a** | 67 |
| 4 | H | $Pr^iCH_2$ | H | | **12c** | hexane | 12 | 50/50 | **13c** | 27 |
| 5 | H | Pentyl | H | | **12d** | hexane | 3 | 50/50 | **13d** | 70 |

a) Determined by VPC.

group, followed by elimination of the silyl group and dehydrochlorination (Scheme 6).

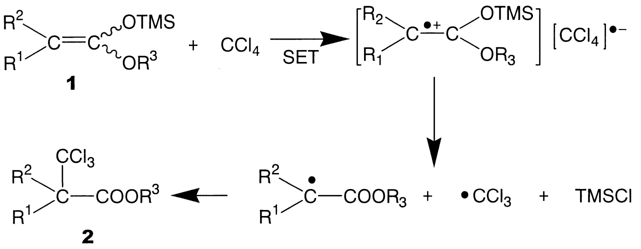


Scheme 6.

The reactions of **12a** and **12d** with $BrCCl_3$ in a hexane solution afforded products of ketone-type bearing a trichloromethyl group at the $\alpha$-position (i.e., **16a** and **16b**) (Table 7), in contrast to the reaction with $CCl_4$ (cf. Table 6). In the reaction with $CBr_4$ in a hexane solution, **12a**, **12e**, and **12f** gave products **17a**, **17b**, and **17c**, respectively, through the addition of a tribromomethyl group, followed by dehydrobromination (Table 8), similarly to the reaction using aldehyde-derived silyl enol ethers (cf. Table 5, run 1 and Scheme 4). 1,1,1-Trichloro-2,2,2-trifluoroethane gave the ketone derivatives **18a** and **18b** bearing a $CCl_2CF_3$ group at the $\alpha$-position by reactions with **12a** and **12e** in a hexane solution, respectively (Table 9).

## Discussion

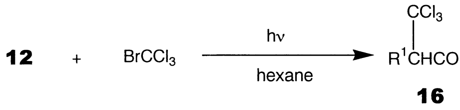
Ketene silyl acetals and silyl enol ethers are known to undergo an attack of electrophiles to give $\alpha$-functionalized carbonyl derivatives. However, the generation of an electrophilic species carrying a positive charge from the polyhalides may be difficult under our conditions without a Lewis acid promoter, although alkyl or vinyl monohalides (particularly iodides) have been reported to generate ionic species, i.e., carbocations and halide anions, under photo-irradiation conditions.[10] Thus, it would be reasonable to assume that polyhaloalkyl radicals are the working intermediates in an attack on the ketene silyl acetals or silyl enol ethers in our reactions using polyhalides. Because a spontaneous bond scission of $CCl_4$ at ambient temperature, or under reflux conditions, is difficult, the formations of **2a** and **2b** might be derived from the reactions of trichloromethyl radicals generated through a single electron transfer (SET) process between $CCl_4$ and the ketene silyl acetals, **1a** and **1b**, bearing strongly electron-donating substituents (Scheme 7).



Scheme 7.

The finding that the yield of **2a** in the reaction of **1a** in a polar solvent (THF) was better than that in a non-polar solvent (hexane) (34 and 2%, respectively; Table 3, runs 1 and 6) would provide some support for the SET hypothesis. The reaction of ketene silyl acetals under photo-irradiation conditions might also include the SET process, as suggested by the result that the formation of **2c** from **1c** was enhanced by the addition of $LiClO_4$[11] (Table 10, runs 1 and 2).

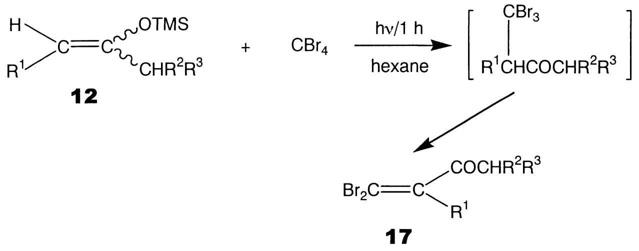
Table 7. Photoreaction of Ketone-Derived Silyl Enol Ethers with $BrCCl_3$ in a Hexane Solution



| Run | Substrate | Time/h | Product | | | | Yield^a)/% |
|---|---|---|---|---|---|---|---|
| | | | $R^1$ | $R^2$ | $R^3$ | | |
| 1 | **12a** | 6 | Me | Me | H | **16a** | 55 |
| 2 | **12d** | 3 | H | penty | H | **16b** | 64 |

a) Determined by VPC.

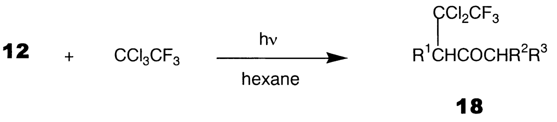
Table 8. Photo-reaction of Ketone-Derived Silyl Enol Ethers with $CBr_4$ in a Hexane Solution



| Run | Substrate | | | | | Product | Yield^a)/% |
|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | *E/Z* | | | |
| 1 | Me | Me | H | 45/55 | **12a** | **17a** | 73 |
| 2 | pentyl | H | H | 44/56 | **12e** | **17b** | 79 |
| 3 | H | Me | Me | | **12f** | **17c** | 70 |

a) Determined by VPC.

Table 9. Photo-Reaction of Ketone-Derived Silyl Enol Ethers with $CCl_3CF_3$ in a Hexane Solution



| Run | Substrate | Time/h | Product | | | | Yield^a)/% |
|---|---|---|---|---|---|---|---|
| | | | $R^1$ | $R^2$ | $R^3$ | | |
| 1 | **12a** | 12 | Me | Me | H | **18a** | 70 |
| 2 | **12e** | 24 | pentyl | H | H | **18b** | 72 |

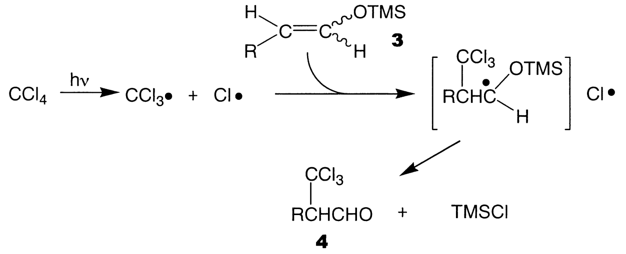
a) Determined by VPC.

Table 10. Effects of $LiClO_4$ on the Reaction of **1c** or **3b** with $CCl_4$ in a THF Solution^a)

| Run | Substrate | Conditions | Product | Yield^b)/% |
|---|---|---|---|---|
| 1 | **1c** | 3.5 h/*hv*/$LiClO_4$ | **2c** | 32 |
| 2 | **1c** | 3.5 h/*hv* | **2c** | 14 |
| 3 | **3b** | 1 h/*hv*/$LiCLO_4$ | **4b** | 0 |
| 4 | **3b** | 1 h/*hv* | **4b** | 68 |

a) **1c** or **3b** (2 mmol), $CCl_4$ (4 mmol), $LiClO_4$ (2 mmol), and THF (5 mL).
b) Determined by VPC.

However, the homolytic scission of a carbon–chlorine bond might preferentially operate in the photoreaction of the aldehyde-derived silyl enol ether (Scheme 8), as suggested by the result that the formation of the trichloromethylated product **4b** from **3b** was rather enhanced by the reaction in a non-polar solvent (hexane) compared with that in a polar solvent (Table 3, runs 8–12) and suppressed by the addition of $LiClO_4$ (Table 10, runs 3 and 4). Furthermore, the observation that the photoreaction of **3b** (1 eq.) with $CCl_4$ (2 eq.) in a $Et_2O$ solution in the presence of a radical quencher (i.e., hydroquinone, 1 equiv) for 1 h deterred the formation of **4b** (5% yield, cf. Table 3 run 9) may suggest the operation of a radical pathway in our reaction. Indeed, the photoreaction of polyhaloalkanes, such as carbon tetrachloride, with olefins to form the 1 : 1 adducts has been reported to be initiated by the homolytic scission of a carbon–halogen bond, followed by the addition of the resulting polyhaloalkyl radicals to olefins.[12]



Scheme 8.

While the reaction of **12** with $CCl_4$ furnished the ketone-derived silyl enol ether **13** through the addition of a trichloromethyl group, followed by migration of the carbon-carbon double bond without the elimination of the silyl group, the reaction with $BrCCl_3$ formed the ketone-type product **16** through the elimination of the silyl group. Based on the hypothesis that the homolytic scission of a carbon-halogen bond would be a trigger step in photo-reaction of silyl enol ethers with polyhalides, this difference in the type of product might be explained by the rationalization that, while a chlorine radical abstracts a hydrogen atom from the methylene group $\alpha$ to the radical center of the intermediate generated by the addition of a trichloromethyl radical to **12** to afford the silyl enol ether derivative **13** in the reaction with $CCl_4$, the reaction with $BrCCl_3$ results in the formation of the ketone-type product **16** via abstraction of the trimethylsilyl group, not a hydrogen atom, by a bromine radical from the same intermediate, which might be ascribed to a lower dissociation energy of a H–Br bond compared with a H–Cl bond.[13] The reaction of **12** with $CBr_4$ and 1,1,1-trichloro-2,2,2-trifluoroethane furnished the ketone-type products **17** and **18**, respectively, contrary to formation of the silyl enol ether derivatives in a reaction with $CCl_4$. The formation of **17** might be due to the diminished ability of a bromine radical to abstract a hydrogen, as in the reaction using $BrCCl_3$, and the steric encumbrance of an intermediate generated by the addition of the 1,1-dichloro-2,2,2-trifluoroethyl radical to **12** might operate as a driving force for the formation of **18**.

## Conclusion

The reactions of ketene silyl acetals and sikyl enol ethers with polyhaildes were successfully performed without a promoter. Ketene silyl acetals were reacted in a $CCl_4$ solution under ambient temperature, reflux or photo-irradiation conditions to afford esters bearing trichloromethyl substituents at the $\alpha$-position. Aldehyde-derived silyl enol ethers were also reacted with $CCl_4$ under photo-irradiation conditions to afford $\alpha$-trichloromethylated aldehydes and, furthermore, reacted with polyhalides other than $CCl_4$ in a hexane solution to give aldehydes having polyhaloalkyl substituents at the $\alpha$-position. The use of $CH_2I_2$ as a polyhalide resulted in the formation of an $\alpha$-iodo aldehyde, and the use of a monoiodine- containing compound furnished a product of aldol-condensation type. The photoreactions of ketone-derived silyl enol ethers with $CCl_4$ afforded sillyl enol ethers derived upon the addition of addition of a trichloromethyl group, followed by migration of the carbon-carbon double bond, whereas polyhalides other than $CCl_4$ (i.e., $BrCCl_3$, $CBr_4$, or $CCl_3CF_3$) gave ketones having polyhaloalkyl substituents at the $\alpha$-position or conjugated enones based on their dehydrohalogenation.

## Experimental

**Instrumental.** IR spectra were recorded on a Horiba FT-210 spectrometer. $^{1}H$ (60 MHz) and $^{13}C$ (15 MHz) NMR spectra were recorded using a JEOL FX60 spectrometer for $CDCl_3/CCl_4$ solutions; the chemical shift ($\delta$) is expressed in ppm relative to tetramethylsilane as an internal standard and the coupling constant ($J$) is expressed in Hz. Mass spectra were obtained at 70 eV using a Hitachi M-80b instrument equipped with a 10 m megabore DB-1 column. VPC was carried out in 10% silicon SE-30 on chromosorb using Shimadzu GC-12A. Preparative TLC was performed on Merck 60F254 silica gel.

**Preparation of Silyl Substrates.** Ketene silyl acetals **1a** and **1b** were prepared according to methods of Kita[14] and Wissner,[15] respectively, and ketene silyl acetals **1c–g** were prepared according to a method of Ainsworth.[16] Silyl enol ethers were prepared according to a method of House.[17]

**Reaction in a $CCl_4$ Solution.** A solution consisting of a silyl substrate (2 mmol) and $CCl_4$ (10 mL) was stirred at ambient or reflux temperature under an $N_2$ atmosphere, or irradiated using a high-pressure Hg lamp (500 W) in a quartz tube under an $N_2$ atmosphere. The residue after removal of $CCl_4$ under reduced pressure was purified by preparative VPC or TLC.

**Reaction in a Hexane Solution.** A solution of a silyl substrate (2 mmol), a polyhalide (4 mmol) and hexane (5 mL) was irradiated using a high-pressure Hg lamp in a quartz tube under an $N_2$ atmosphere. After the reaction mixture had been concentrated under reduced pressure, the product was isolated by preparative VPC or TLC.

**Methyl 3,3,3-Trichloro-2-dimethylaminopropionate 2a.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 1758; $^{1}H$ NMR $\delta$ 3.95 (1H, s, C(2)H), 3.85 (3H, s, COOMe), 2.75 (6H, s, NMe); $^{13}C$ NMR $\delta$ 80.26, 51.17, 44.10; MS (EI) $m/z$ 235 [M($^{37}$Cl)$^{+}$, 13%], 233 (M$^{+}$, 12), 200 (80), 198 (90), 178 (70), 176 (90), 174 (90), 116 (100). Found: M$^{+}$ 232.9794: $C_6H_{10}Cl_3NO_2$ requires 232.9776.

**Methyl 3,3,3-Trichloro-2-Methoxypropionate 2b.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 1760; $^{1}H$ NMR $\delta$ 4.28 (1H, s, C(2)H), 3.85 (3H, s, COOMe), 3.67 (3H, s, OMe); $^{13}C$ NMR $\delta$ 89.66, 59.89, 52.38; MS (EI) $m/z$ 165 (17%), 163 (62), 161 (63), 103 (100); MS (CI) $m/z$ 223 [M($^{37}$Cl) + 1]$^{+}$, 221 (M + 1)$^{+}$. Found: (M-COOMe)$^{+}$ 160.9331: $C_3H_4Cl_3O$ requires 160.9328.

**Methyl 3,3,3-Trichloro-2-methylpropionate 2c.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1743; $^{1}$H NMR $\delta$ 3.76 (3H, s, COOMe), 3.52 (1H, q, $J$ = 6.9 Hz, C(2)H), 1.66 (3H, d, $J$ = 6.9 Hz, C(3)H); $^{13}$C NMR $\delta$ 59.55, 51.95, 15.25; MS (EI) *m/z* 173 (22%), 171 (43), 169 (61), 145 (30), 112 (40), 110 (60), 59 (100); MS (CI) *m/z* 207 [M ($^{37}$Cl) + 1]$^{+}$, 205 [M + 1]$^{+}$. Found: (M − Cl)$^{+}$ 168.9842: $C_5H_7Cl_2O_2$ requires 168.9823.

**Ethyl 2-(Trichloromethyl)butanoate 2d.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1745; $^{1}$H NMR $\delta$ 4.23 (2H, q, $J$ = 6.9 Hz, $COOCH_2$), 3.49 (1H, t, $J$ = 6.9 Hz, C(2)H), 2.28–1.88 (2H, m, C(3)H), 1.35 (3H, t, $J$ = 6.9 Hz, $COOCH_2CH_3$), 1.05 (3H, t, $J$ = 5.2 Hz, C(4)H); $^{13}$C NMR $\delta$ 67.22, 61.06, 23.55, 14.03, 11.41; MS (EI) *m/z* 191 (10%), 189 (29), 187 (29), 171 (45), 169 (75), 126 (48), 124 (82), 89 (100); MS (CI) *m/z* 235 [M($^{37}$Cl) + 1]$^{+}$, 233 (M + 1)$^{+}$. Found: (M − OEt)$^{+}$ 186.9501: $C_5H_6Cl_3O$ requires 186.9484.

**Ethyl 2-(Trichloromethyl)hexanoate 2e.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1745; $^{1}$H NMR $\delta$ 4.18 (2H, q, $J$ = 6.9 Hz, $COOCH_2$), 3.46 (1H, t, $J$ = 6.9 Hz, C(2)H), 2.32–1.80 (m, 2H, C(3)H), 2.68–2.26 (m, 4H, C(4)H, C(5)H), 2.39 (t, 3H, $J$ = 6.9 Hz, $COOCH_2CH_3$), 0.98 (t, 3H, $J$ = 5.1 Hz, C(6)H); $^{13}$C NMR $\delta$ 65.44, 60.96, 29.73, 28.90, 22.07, 14.03, 13.64; MS (EI) *m/z* 219 (6%), 217 (18), 215 (18), 171 (95), 169 (95), 143 (63), 141 (58), 56 (100); MS (CI) *m/z* 263 [M($^{37}$Cl) + 1]$^{+}$, 261 (M + 1)$^{+}$. Found: (M − OEt)$^{+}$ 214.9804: $C_7H_{10}Cl_3O$ requires 214.9796.

**Methyl 3,3,3-Trichloro-2,2-dimethylpropionate 2f.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1743; $^{1}$H NMR $\delta$ 3.80 (3H, s, COOMe), 1.70 (6H, s, C(2)-Me); $^{13}$C NMR $\delta$ 52.38, 23.20; MS (EI) *m/z* 191 (3%), 189 (12), 187 (12), 126 (52), 124 (85), 101 (90), 59 (100); MS (CI) *m/z* 221 [M($^{37}$Cl) + 1]$^{+}$, 219 (M + 1)$^{+}$. Found: (M − OMe)$^{+}$ 186.9470: $C_5H_6Cl_3O$ requires 186.9483.

**Ethyl 3,3-Dimethyl-2-(trichloromethyl)butanoate 2g.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1741; $^{1}$H NMR $\delta$ 4.18 (2H, q, $J$ = 6.9 Hz, $COOCH_2$), 3.47 (1H, s, C(2)H), 1.33 (3H, t, $J$ = 6.9 Hz, $COOCH_2CH_3$), 1.33 (9H, s, C(3)-Me, C(4)H); $^{13}$C NMR $\delta$ 72.85, 60.82, 30.02, 14.03; MS (EI) *m/z* 125 (37%), 123 (56), 57 (100); MS (CI) *m/z* 263 [M($^{37}$Cl) + 1]$^{+}$, 261 (M + 1)$^{+}$. Found: (M − *t*-Bu − OEt − Cl)$^{+}$ 122.9422: $C_3HCl_2O$ requires 122.9405.

**2-(Trichloromethyl)butanal 4a.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1730; $^{1}$H NMR $\delta$ 9.82 (1H, d, $J$ = 3.8 Hz, CHO), 3.40–3.00 (1H, m, C(2)H), 2.42–1.83 (2H, m, C(3)H), 1.10 (3H, t, $J$ = 6.8 Hz, C(4)H); $^{13}$C NMR $\delta$ 195.08, 71.69, 21.23, 11.29; MS (EI) *m/z* 154 (4%), 152 (7), 125 (43), 89 (100); MS (CI) *m/z* 191 [M($^{37}$Cl) + 1]$^{+}$, 189 (M + 1)$^{+}$. Found: (M − HCl)$^{+}$ 151.9774: $C_5H_6Cl_2O$ requires 151.9794.

**2-(Trichloromethyl)heptanal 4b.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1724; $^{1}$H NMR $\delta$ 9.82 (1H, d, $J$ = 3.8 Hz, CHO), 3.38–3.09 (1H, m, C(2)H), 2.37–1.80 (2H, m, C(3)H), 1.70–1.14 (6H, m, C(4)H-C(6)H), 0.97 (3H, t, $J$ = 5.1 Hz, C(7)H); $^{13}$C NMR $\delta$ 193.57, 65.40, 31.14, 30.16, 26.56, 22.22, 13.84; MS (EI) *m/z* 159 (6%), 127 (70), 125 (100); MS (CI) *m/z* 233 [M($^{37}$Cl) + 1]$^{+}$, 231 (M + 1)$^{+}$. Found: (M − HCl − Cl)$^{+}$ 159.0555: $C_8H_{12}ClO$ requires 159.0575.

**2-(Trichloromethyl)octanal 4c.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1725; $^{1}$H NMR $\delta$ 9.84 (1H, d, $J$ = 3.8 Hz, CHO), 3.37–2.98 (1H, m, C(2)H), 2.30–1.76 (2H, m, C(3)H), 1.60–1.10 (8H, m, C(4)H-C(7)H), 0.97 (3H, t, $J$ = 5.1 Hz, C(8)H); $^{13}$C NMR $\delta$ 195.57, 69.54, 31.23, 28.67, 27.76, 26.47, 22.33, 13.85; MS (EI) *m/z* 175 (6%), 173 (16), 127 (43), 125 (83), 43 (100); MS (CI) *m/z* 247 [M($^{37}$Cl) + 1]$^{+}$, 245 (M + 1)$^{+}$. Found: (M − HCl − Cl)$^{+}$ 173.0755: $C_9H_{14}ClO$ requires 173.0732.

**1,1,1,3-Tetrachloro-3-methyl-2-(trimethylsiloxy)butane 6.** A colorless oil; $^{1}$H NMR $\delta$ 4.45 (1H, s, C(2)H), 2.00 (3H, s, C(3)-MeAMeB), 1.88 (3H, s, C(3)-MeAMeB), 0.20 (9H, s, SiMe); $^{13}$C NMR $\delta$ 89.24, 31.60, 28.79, 0.43; MS (EI) *m/z* 221 (45%), 219 (47), 143 (75), 93 (100), 73 (85); MS (CI) *m/z* 299 [M($^{37}$Cl) + 1]$^{+}$, 297 (M + 1)$^{+}$. Found: (M − $CClMe_2$)$^{+}$ 218.9686: $C_5H_{10}Cl_3OSi$ requires 218.9566.

**2-(Pentachloroethyl)heptanal 7a.** Mp 96–98 °C; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1728; $^{1}$H NMR $\delta$ 9.92 (1H, d, $J$ = 3.9 Hz, CHO), 3.32–2.97 (1H, m, C(2)H), 2.25–1.78 (2H, m, C(3)H), 1.68–1.12 (6H, m, C(4)H-C(6)H), 0.98 (3H, t, $J$ = 5.1 Hz, C(7)H); $^{13}$C NMR $\delta$ 194.23, 58.36, 30.96, 29.83, 25.72, 23.64, 13.80; MS (EI) *m/z* 245 (1%), 243 (7), 241 (7), 129 (30), 127 (100), 125 (100); MS (CI) *m/z* 315 [M($^{37}$Cl) + 1]$^{+}$, 313 (M + 1)$^{+}$. Found: (M − HCl − Cl)$^{+}$ 240.9934: $C_9H_{12}Cl_3O$ requires 240.9952.

**2-(1,1-Dichloro-2,2,2-trifluoroethyl)heptanal 7b.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1730; $^{1}$H NMR $\delta$ 9.78 (1H, d, $J$ = 3.8 Hz, CHO), 3.30–2.84 (1H, m, C(2)H), 2.24–1.75 (2H, m, C(3)H), 1.66–1.12 (6H, m, C(4)H-C(6)H), 0.96 (3H, t, $J$ = 5.1 Hz, C(7)H); $^{13}$C NMR $\delta$ 194.23, 59.23, 31.11, 25.93, 24.57, 22.08, 13.73; MS (EI) *m/z* 266 [M($^{37}$Cl)$^{+}$, 13%], 264 (M$^{+}$, 26), 161 (68), 159 (100). Found: M$^{+}$ 264.0296: $C_9H_{13}Cl_2F_3O$ requires 264.0294.

**2-(1,2-Dichloro-1,2,2-trifluoroethyl)heptanal 7c.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1728; $^{1}$H NMR $\delta$ 9.76 (1H, d, $J$ = 3.8 Hz, CHO), 3.35–3.00 (1H, m, C(2)H), 2.28–1.80 (2H, m, C(3)H), 1.69–1.18 (6H, m, C(4)H-C(6)H), 0.95 (3H, t, $J$ = 5.1 Hz, C(7)H); $^{13}$C NMR $\delta$ 193.26, 58.11, 30.24, 28.78, 25.36, 23.58, 13.81; MS (EI) *m/z* 266 [M($^{37}$Cl)$^{+}$, 8%], 264 (M$^{+}$, 13), 205 (90), 203 (100), 181 (10), 179 (33), 177 (71), 175 (88), 169 (62), 167 (98). Found: M$^{+}$ 264.0276: $C_9H_{13}Cl_2F_3O$ requires 264.0294.

**2-(2-Bromo-1-chloro-1,2,2-trifluoroethyl)heptanal 7d.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1728; $^{1}$H NMR $\delta$ 9.80 (1H, d, $J$ = 3.8 Hz, CHO), 3.36–3.00 (1H, m, C(2)H), 2.30–1.80 (2H, m, C(3)H), 1.65–1.15 (6H, m, C(4)H-C(6)H), 0.98 (3H, t, $J$ = 5.1 Hz, C(7)H); $^{13}$C NMR $\delta$ 195.16, 57.77, 31.23, 26.05, 23.97, 22.08, 13.73; MS (EI) *m/z* 310 [M($^{37}$Cl)$^{+}$, 14%], 308 (M$^{+}$, 10), 240 (42), 238 (32), 205 (76), 203 (86), 145 (100). Found: M$^{+}$ 307.9802: $C_9H_{13}BrClF_3O$ requires 307.9790.

**2-(Dibromomethylene)heptanal 9a.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1710; $^{1}$H NMR $\delta$ 10.07 (1H, s, CHO), 2.35 (2H, t, $J$ = 6.9 Hz, C(3)H), 1.83–1.15 (6H, m, C(4)H-C(6)H), 0.98 (3H, t, $J$ = 5.1 Hz, C(7)H); $^{13}$C NMR $\delta$ 188.15, 31.48, 31.09, 26.85, 22.22, 13.84; MS (EI) *m/z* 230 (27%), 228 (63), 226 (32), 205 (98), 203 (98), 149 (100), 147 (100); MS (CI) *m/z* 285 [M($^{37}$Cl) + 1]$^{+}$, 283 (M + 1)$^{+}$. Found: (M − Br)$^{+}$ 203.0045: $C_8H_{12}BrO$ requires 203.0070.

**(Z)-2-(Bromomethylene)heptanal 9b.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 3025, 1705; $^{1}$H NMR $\delta$ 9.90 (1H, s, CHO), 7.34 (1H, s, C(1)H), 2.35 (2H, t, $J$ = 6.9 Hz, C(3)H), 1.79–1.13 (6H, m, C(4)H-C(6)H), 0.96 (3H, t, $J$ = 5.1 Hz, C(7)H); $^{13}$C NMR $\delta$ 189.17, 132.25, 34.52, 31.35, 26.71, 22.20, 13.30; MS (EI) *m/z* 206 [M($^{81}$Br)$^{+}$, 5%], 204 (M$^{+}$, 5), 150 (33), 148 (34), 125 (100). Found: M$^{+}$ 204.0173: $C_8H_{13}BrO$ requires 204.0150.

**2-(Dibromomethylene)nonanal 10.** A colorless oil; IR $\nu_{\max}$ (neat)/cm$^{-1}$ 1710; $^{1}$H NMR $\delta$ 10.10 (1H, s, CHO), 2.38 (2H, t, $J$ = 6.9 Hz, C(3)H), 1.82–1.15 (10H, m, C(4)H-C(8)H), 0.97 (3H, t, $J$ = 5.1 Hz, C(9)H); $^{13}$C NMR $\delta$ 189.17, 31.72, 31.29, 29.40, 28.91, 27.33, 22.63, 14.09; MS (EI) *m/z* 233 (57%), 231 (52), 152 (100); MS (CI) *m/z* 313 [M($^{81}$Br) + 1]$^{+}$, 311 (M + 1)$^{+}$. Found: (M − Br)$^{+}$ 231.0368: $C_{10}H_{16}BrO$ requires 231.0384.

**5,5-Dibromo-2,4-pentadienal 11.** A colorless oil; IR $\nu_{\max}$

(neat)/cm$^{-1}$ 1700; $^{1}$H NMR $\delta$ 10.10 (1H, d, $J$ = 6.8 Hz, CHO), 7.22 (3H, br s, C(2)H-C(4)H); $^{13}$C NMR $\delta$ 192.77, 145.73, 134.87, 133.29; MS (EI) $m/z$ 240 [M($^{81}$Br)$^+$, 30%], 238 (M$^+$, 15), 211 (14), 209 (7), 161 (100), 159 (100). Found: M$^+$ 237.8611: $C_5H_4Br_2O$ requires 237.8630.

**5,5,5-Trichloro-4-methyl-3-trimethylsiloxy-2-pentene (*E*,*Z* mixture) 13a.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 3040, 1668; $^{1}$H NMR $\delta$ 5.00–4.48 (1H, m, C(2)H), 3.32–2.90 (1H, m, C(4)H), 1.64 (6H, t, $J$ = 1.76 Hz, C(1)H, C(4)-Me), 0.23 (9H, s, SiMe); $^{13}$C NMR $\delta$ 105.56, 102.92, 60.60, 53.92, 16.18, 14.83, 12.13, 10.78, 0.97; MS (EI) $m/z$ component A 276 [M($^{37}$Cl)$^+$, 20%], 274 (M$^+$, 20), 157 (63), 91 (100), 73 (81); component B 276 [M(37Cl)$^+$, 17%], 274 (M$^+$, 7), 157 (79), 91 (65), 73 (100). Found: M$^+$ 274.0091: $C_9H_{17}Cl_3OSi$ requires 274.0112.

**5-Trichloromethyl-4-trimethylsiloxy-3-heptene (*E*,*Z* mixture) 13b.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 3039, 1660; $^{1}$H NMR $\delta$ 4.98–4.52 (1H, m, C(3)H), 3.37–3.15 (1H, m, C(5)H), 2.32–1.80 (4H, m, C(2)H, C(6)H), 1.04 (3H, t, $J$ = 6.9, C(1)H or C(7)H), 1.02 (3H, t, $J$ = 6.9, C(1)H or C(7)H), 0.22 (9H, s, SiMe); $^{13}$C NMR $\delta$ 115.44, 112.91, 68.03, 60.86, 22.27, 21.10, 20.03, 19.00, 14.47, 13.09, 11.94, 11.50, 0.97; MS (EI) $m/z$ component A 304 [M($^{37}$Cl)$^+$, 64%], 302 (M$^+$, 63), 269 (35), 267 (54), 241 (65), 239 (100), 185 (100), 73 (85); component B 304 [M($^{37}$Cl)$^+$, 25%], 302 (M$^+$, 25), 241 (34), 269 (15), 267 (25), 241 (34), 239 (54), 185 (100), 73 (95). Found: M$^+$ 302.0404: $C_{11}H_{21}Cl_3OSi$ requires 302.0425.

**1,1,1-Trichloro-6-Methyl-3-trimethylsiloxy-3-heptene (*E*,*Z* mixture) 13c.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 3037, 1660; $^{1}$H NMR $\delta$ 4.92–4.51 (1H, m, C(4)H), 3.02 (2H, s, C(2)H), 3.00 (2H, s, C(2)H), 2.28–1.78 (2H, m, C(5)H), 1.00 (6H, d, $J$ = 6.9 Hz, C(7)H, C(6)-Me), 0.21 (9H, s, SiMe); $^{13}$C NMR $\delta$ 114.52, 112.08, 52.02, 44.94, 36.82, 35.80, 31.04, 29.96, 22.20, 21.17, 0.97; MS (EI) $m/z$ component A 304 [M($^{37}$Cl)$^+$, 8%], 302 (M$^+$, 8), 261 (30), 259 (30), 93 (100), 73 (88), 54 (82); component B 304 [M($^{37}$Cl)$^+$, 15%], 302 (M$^+$, 15), 261 (62), 259 (63), 93 (90), 73 (93), 54 (100). Found: M$^+$ 302.0411: $C_{11}H_{21}Cl_3OSi$ requires 302.0425.

**1,1,1-Trichloro-3-trimethylsiloxy-3-nonene (*E*,*Z* mixture) 13d.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 3036, 1660; $^{1}$H NMR $\delta$ 4.94–4.52 (1H, m, C(4)H), 3.06 (2H, s, C(2)H), 3.02 (2H, s, C(2)H), 2.32–1.81 (2H, m, C(5)H), 1.70–1.19 (6H, m, C(6)H-C(8)H), 0.97 (3H, t, $J$ = 5.1 Hz, C(9)H); $^{13}$C NMR $\delta$ 116.62, 114.37, 50.43, 43.85, 32.82, 32.46, 30.32, 29.27, 28.31, 27.29, 26.77, 13.91, 0.97; MS (EI) $m/z$ component A 303 (21%), 301 (21), 199 (89), 73 (100); component B 303 (17%), 301 (16), 199 (76), 73 (100); MS (CI) $m/z$ component A 319 [M($^{37}$Cl) + 1]$^+$, 317 (M + 1)$^+$; component B 319 [M($^{37}$Cl) + 1]$^+$, 317 (M + 1)$^+$. Found (M − Me)$^+$ 301.0371: $C_{11}H_{20}Cl_3OSi$ requires 301.0348.

**1,1-Dichloro-4,4-dimethyl-1-penten-3-one 15.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 3056, 1697; $^{1}$H NMR $\delta$ 6.90 (1H, s, C(2)H), 1.22 (9H, s, C(4)-Me, C(5)H); $^{13}$C NMR $\delta$ 122.25, 25.93; MS (EI) $m/z$ 182 [M($^{37}$Cl)$^+$, 10%], 180 (M$^+$, 16), 154 (40), 152 (70), 125 (68), 123 (92), 57 (100). Found: M$^+$ 180.0135: $C_7H_{10}Cl_2O$ requires 180.0108.

**1,1,1-Trichloro-2-methyl-3-pentanone 16a.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 1715; $^{1}$H NMR $\delta$ 3.31 (1H, q, $J$ = 6.9 Hz, C(2)H), 2.40 (2H, q, $J$ = 6.9 Hz, C(4)H), 1.55 (3H, d, $J$ = 6.9 Hz, C(2)-Me), 1.12 (3H, t, $J$ = 6.9 Hz, C(5)H); $^{13}$C NMR $\delta$ 63.87, 36.54, 15.87, 7.38; MS (EI) $m/z$ 177 (4%), 175 (10), 173 (10), 149 (7), 147 (20), 145 (20), 114 (10), 112 (95), 110 (100); MS (CI) $m/z$ 205 [M($^{37}$Cl) + 1]$^+$, 203 (M + 1)$^+$. Found: (M − Et)$^+$ 172.9346: $C_4H_4Cl_3O$ requires 172.9330.

**1,1,1-Trichloro-3-nananone 16b.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 1715; $^{1}$H NMR $\delta$ 3.25 (2H, s, C(2)H), 2.35 (2H, t, $J$ = 6.9 Hz, C(4)H), 1.62–1.20 (8H, m, C(5)H-C(8)H), 0.95 (3H, t, C(9)H); $^{13}$C NMR $\delta$ 66.35, 42.08, 31.54, 28.79, 23.73, 22.45, 13.91; MS (EI) $m/z$ 170 (2%), 168 (9), 166 (15), 143 (4), 141 (20), 139 (38), 95 (74), 70 (100); MS (CI) $m/z$ 247 [M($^{37}$Cl) + 1]$^+$, 245 (M + 1)$^+$. Found: (M − Cl − $CH_2CH_2CH_3$) 165.9936: $C_6H_8Cl_2O$ requires 165.9952.

**1,1-Dibromo-2-methyl-1-penten-3-one 17a.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 1688; $^{1}$H NMR $\delta$ 2.82 (2H, q, $J$ = 6.9 Hz, C(4)H), 2.08 (3H, s, C(2)-Me) 1.14 (3H, t, $J$ = 6.9 Hz, C(5)H); $^{13}$C NMR $\delta$ 33.6, 12.7, 10.13; MS (EI) $m/z$ 256 [M($^{81}$Br)$^+$, 40%], 254 (M$^+$, 19), 229 (50), 227 (100), 225 (50), 201 (28), 199 (60), 197 (50). Found: M$^+$ 253.8923: $C_6H_8Br_2O$ requires 253.8943.

**3-(Dibromomethylene)-2-octanone 17b.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 1690, 1570; $^{1}$H NMR $\delta$ 2.35 (2H, t, $J$ = 6.9 Hz, C(3)H), 2.30 (3H, s, COMe), 1.74–1.15 (6H, m, C(4)H-C(6)H), 0.98 (3H, t, $J$ = 5.1 Hz, C(7)H); $^{13}$C NMR $\delta$ 33.24, 31.82, 26.00, 22.37, 21.16, 13.92; MS (EI) $m/z$ 219 (50%), 217 (50), 138 (73), 95 (60), 39 (100); MS (CI) $m/z$ 299 [M($^{81}$Br) + 1]$^+$, 297 (M + 1)$^+$. Found: (M − Br)$^+$ 217.0213: $C_9H_{14}BrO$ requires 217.0228.

**1,1-Dibromo-4-methyl-1-penten-3-one 17c.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 3030, 1692; $^{1}$H NMR $\delta$ 7.28 (1H, s, C(2H), 3.11–2.65 (1H, m, C(4)H), 1.18 (6H, d, $J$ = 6.5 Hz, C(4)-Me, C(5)H); $^{13}$C NMR $\delta$ 137.25, 38.26, 16.93; MS (EI) $m/z$ 215 (38%), 213 (80), 211 (40), 175 (28), 177 (28), 134 (80), 132 (83), 52 (100); MS (CI) $m/z$ 257 [M($^{81}$Br) + 1]$^+$, 255 [M + 1]$^+$. Found: (M − $CHMe_2$)$^+$ 210.8378: $C_3HBr_2$ Orequires 210.8395.

**5,5-Dichloro-6,6,6-trifluoro-4-methyl-3-hexanone 18a.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 1715; $^{1}$H NMR $\delta$ 3.45 (1H, q, $J$ = 6.9 Hz, C(4)H), 2.41 (2H, q, $J$ = 6.9 Hz, C(2)H), 1.60 (3H, d, $J$ = 6.9 Hz, C(4)-Me), 1.12 (3H, t, $J$ = 6.9 Hz, C(1)H); $^{13}$C NMR $\delta$ 52.63, 36.74, 13.74, 7.46; MS (EI) $m/z$ 301 (2%), 209 (12), 207 (20), 183 (5), 181 (24), 179 (41), 75 (100); MS (CI) $m/z$ 239 [M($^{37}$Cl) + 1]$^+$, 237 (M + 1)$^+$. Found: (M − Et)$^+$ 206.9574: $C_5H_4Cl_2F_3O$ requires 206.9591.

**3-[1,1-Dichloro-2,2,2-trifluoroethyl]-2-octanone 18b.** A colorless oil; IR $\nu_{max}$ (neat)/cm$^{-1}$ 1715; $^{1}$H NMR $\delta$ 3.42 (1H, q, $J$ = 6.9 Hz, C(3)H), 2.25–1.76 (2H, m, C(4)H), 2.16 (3H, s, C(1)H), 1.64–1.12 (6H, m, C(5)H-C(7)H), 0.96 (3H, t, $J$ = 5.1 Hz, C(8)H); $^{13}$C NMR $\delta$ 64.22, 32.16, 25.89, 23.67, 23.42, 22.95, 13.71; MS (EI) $m/z$ 280 [M($^{37}$Cl)$^+$, 5%], 278 (M$^+$, 8), 211 (5), 209 (24), 207 (40), 174 (20), 172 (75), 113 (100). Found: M$^+$ 278.0464: $C_{10}H_{15}Cl_2F_3O$ requires 278.0451.

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