



## Chlorination of various substrates in subcritical carbon tetrachloride

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### ARTICLE INFO

#### Article history:

Received 17 December 2009

Received in revised form 2 February 2010

Accepted 2 February 2010

Available online 10 February 2010

#### Keywords:

Subcritical conditions

Carbon tetrachloride

Chlorination

Radical reactions

### ABSTRACT

Various aliphatic hydrocarbons and the side chains of aromatic hydrocarbons were chlorinated in subcritical carbon tetrachloride. Chlorination of aromatic compounds including 1,4-disubstituted benzenes was investigated. Ketones and sulfones were stable under the employed conditions. Sulfoxides were converted into sulfides in a low to modest yields. The coupling adducts between olefins and carbon tetrachloride were obtained from the reactions of olefins.

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### 1. Introduction

Much attention has been paid to supercritical and subcritical water as a medium for chemical reactions, since it has quite unique properties such as low polarity and the change of the  $pK_w$  value ( $pK_w=11.2$  at 250 °C).<sup>1</sup> Supercritical alcohols are also attractive solvents because of unique reactivities such as direct addition of alcohols to alkenes.<sup>2</sup>

Direct introduction of halogen substituents into various classes of organic molecules can be achieved by free-radical reactions. Especially, halogenation of aliphatic hydrocarbons and side chains of aromatic hydrocarbons has been reported by many researchers.<sup>3–5</sup>

In our continuing studies concerning the halogenation of organic compounds,<sup>6</sup> we were interested in the chlorination of organic compounds under high temperature conditions. We planned to chlorinate organic substrates by the reactions of chloro radical generated from the C–Cl bond cleavage of carbon tetrachloride under high temperature conditions. We have reported the chlorination of some typical compounds in high temperature carbon tetrachloride as the preliminary communication.<sup>7</sup> As an extension of the work, this paper describes full details of the reactions of a variety of compounds, including the reactions of 1,4-disubstituted benzenes.

### 2. Results and discussions

First, adamantane (**1**) was chosen as the model compound of aliphatic hydrocarbons. The critical temperature of carbon tetrachloride is 283 °C.<sup>8</sup> The reaction was conducted at 250 °C on 7 MPa for 4 h to give 1-chloroadamantane (**2**), 1,3-dichloroadamantane (**3**), and 2-chloroadamantane (**4**) in 52, 9, and 3% yields, respectively (*Caution!*, see [Experimental section](#)) (Table 1, entry 1). Prolonged heating for 9 h gave the dichloro compound **3** in 73% yield together with small amounts of **2** (4%) and **4** (2%) (entry 2). When the reaction was performed at 300 °C, the Teflon crucible equipped in the stainless autoclave melted in spite of the good yield (60%) of **2** (entry 3). We carried out all the reactions at 250 °C because of the above reason. When chloroform and dichloromethane were employed as solvents, monochloride **2** was obtained in low yields (31 and 6% yields, respectively) (entries 4 and 5). Chlorocyclododecane (**6**) and dichlorocyclododecane (**7**) were produced in 35 and 12% yields from the reaction of **5** at 250 °C for 7 h in subcritical carbon tetrachloride, respectively (entry 6). Dichloride **7** was obtained as an inseparable mixture. The positions of the second chlorine atom in **7** are not clear. The reaction of 2,2,3,3-tetramethylbutane (**8**) gave 1-chloro-2,2,3,3-tetramethylbutane (**9**) in a low yield (3%) (entry 7). The relative ease of substitution of hydrogen was tertiary>secondary>primary. The methyl group of *tert*-butylbenzene (**10**) is so unreactive toward ordinary photochemical methods.<sup>9</sup> However, it can be chlorinated with ease by the use of sulfuryl chloride-benzoyl peroxide (BPO) to give 1-chloro-2-methyl-2-phenylpropane (**11**).<sup>9</sup> In contrast, the rearranged product, 2-chloro-2-methyl-1-phenylpropane was yielded by gas-phase photochlorination.<sup>4</sup> Compound **10** was almost unreactive in

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**Table 1**  
The reactions of various hydrocarbons in high temperature solvents<sup>a</sup>

Entry	Substrate	Time (h)	Products (Yield (%) <sup>b</sup> )			Recovery (%) <sup>b</sup>
1		4				(15)
2	<b>1</b>	9	<b>2</b> (4)	<b>3</b> (73)	<b>4</b> (2)	(0)
3 <sup>c</sup>	<b>1</b>	2	<b>2</b> (60)	<b>3</b> (21)	<b>4</b> (4)	(0)
4 <sup>d</sup>	<b>1</b>	4	<b>2</b> (31)	<b>3</b> (0)	<b>4</b> (0)	(49)
5 <sup>e</sup>	<b>1</b>	4	<b>2</b> (6)	<b>3</b> (0)	<b>4</b> (0)	(76)
6		7				(34)
7		7				(95) <sup>f</sup>
8		7				(96) <sup>f</sup>
9	<b>10</b>	21	<b>11</b> (19) <sup>f</sup>			(45) <sup>f</sup>
10		7				(74) <sup>f</sup>
11		7				(42)
12		7				(0)
13		7				(5)
14		4				(32)

<sup>a</sup> Reagents and conditions: Substrates 4.0 mmol, solvent 15 mL, temp 250 °C, N<sub>2</sub>.

<sup>b</sup> Isolated yields.

<sup>c</sup> Temp 300 °C.

<sup>d</sup> Solvent CHCl<sub>3</sub>.

<sup>e</sup> Solvent CH<sub>2</sub>Cl<sub>2</sub>.

<sup>f</sup> The yields were calculated on the basis of the peak of 1,4-dioxane using <sup>1</sup>H NMR spectroscopy.

subcritical carbon tetrachloride (entry 8). Prolonged heating of **10** for 21 h gave chloride **11** in 19% yield accompanying large amounts of polymeric materials (entry 9).

The reactions of the side chains of aromatic hydrocarbons were examined. Toluene (**12**) was chlorinated at the benzylic position in subcritical carbon tetrachloride (entry 10). Reactions of diphenylmethane (**14**) and triphenylmethane (**16**) gave chlorides **15** and **17** in 53 and 99% yields, respectively (entries 11 and 12). The yields of the products were increased with the introduction of the phenyl group, since the resulting radical became more stable. Chlorination of 1-methylnaphthalene (**18**) led to the formation of chloride **19** and dichloride **20** in 36 and 37% yields, respectively (entry 13). We conducted the chlorination of compound **21**, which possesses both of the methine group and the benzylic position. Indeed, chlorination of **21** occurred predominantly at the benzylic position under subcritical conditions (entry 14).

Next, we attempted the reactions of a variety of aromatic compounds at 250 °C for 7 h. The results are summarized in Table 2. Nitrobenzene (**24**) was easily converted into chlorobenzene (**25**) (entry 1). Several reports including photo-initiated chlorination<sup>3</sup> and gas-phase reactions<sup>10</sup> for the transformation of **24** to **25** have been reported. Halogen exchange reactions were investigated. Fluorobenzene (**26**) was recovered without any changes after 7 h (entry 2). Chlorobenzene (**25**) was stable under the employed conditions and further nuclear substitution did not proceed (entry 3). Transformation of bromobenzene (**27**) to chlorobenzene (**25**) proceeded smoothly (entry 4). Many reports have been known for chlorodebromination of bromobenzene (**27**) by photo-induced chlorination,<sup>11–13</sup> the use of sulfonyl chloride-BPO<sup>13</sup> and gas-phase

**Table 2**  
The reactions of nitro and halogen derivatives ArX in high temperature CCl<sub>4</sub><sup>a</sup>

Entry	Substrate	Products (Yield (%) <sup>b</sup> )	Recovery (%) <sup>b</sup>
1			(0)
2		N.R. <sup>f</sup>	(97)
3		N.R. <sup>f</sup>	(99)
4			(0)
5			(0)
6 <sup>c</sup>	<b>28</b>	<b>25</b> (90)	(0)
7 <sup>d</sup>	<b>28</b>	<b>25</b> (31)	(65)
8 <sup>e</sup>	<b>28</b>	<b>25</b> (13)	(84)

<sup>a</sup> Reagents and conditions: Substrates 4.0 mmol, CCl<sub>4</sub> 15 mL, temp 250 °C, time 7 h, N<sub>2</sub>.

<sup>b</sup> The yields were calculated on the basis of the peak of 1,4-dioxane using <sup>1</sup>H NMR spectroscopy.

<sup>c</sup> Temp 240 °C.

<sup>d</sup> Temp 220 °C.

<sup>e</sup> Temp 200 °C.

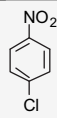
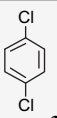
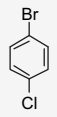
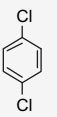
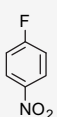
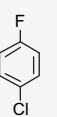
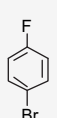
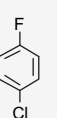
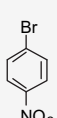
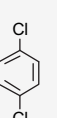
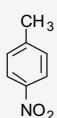
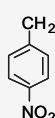
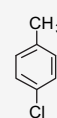
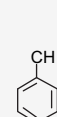
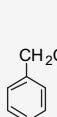
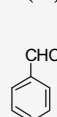
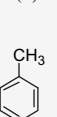
<sup>f</sup> No reaction.

<sup>g</sup> Complex mixture was obtained.

chlorination.<sup>10</sup> Although the yield of chlorobenzene (**25**) was low (50%) at 250 °C because of the production of large amounts of decomposed materials, chlorobenzene (**25**) was obtained at 240 °C in the quantitative yield (90%) from the reaction of iodobenzene (**28**) (entries 5 and 6). It was reported that chlorodeiodination occurred by use of sulfuryl chloride-BPO, while iodobenzene dichloride was produced by photo-induced chlorination of iodobenzene.<sup>11,14,15</sup> Iodobenzene dichloride is the somewhat unstable compound, which decomposes on heating above the melting point (ca. 101–103 °C), affording chiefly *p*-chloriodobenzene.<sup>14b</sup> These materials were not detected by <sup>1</sup>H NMR spectroscopy and T.L.C. in our experiments achieved at 200–250 °C, indicating that iodobenzene (**28**) was transformed to chlorobenzene (**25**), exclusively (entries 5–8).

Chlorination of 1,4-disubstituted benzenes was examined. The results were summarized in Table 3. *p*-Chloronitrobenzene (**29**) and *p*-bromochlorobenzene (**31**) were transformed to *p*-dichlorobenzene (**30**) in 90 and 13% yields, respectively (entries 1 and 2). The nitro and

**Table 3**  
The reactions of *p*-substituted benzenes in high temperature CCl<sub>4</sub><sup>a</sup>

Entry	Substrate	Products (Yield (%) <sup>b</sup> )	Recovery (%) <sup>b</sup>
1		 ( <b>30</b> ) (90)	(0)
2 <sup>c</sup>		 ( <b>30</b> ) (13)	(75)
3		 ( <b>33</b> ) (94)	(0)
4 <sup>d</sup>		 ( <b>33</b> ) (91)	(0)
5		 ( <b>30</b> ) (93)	(0)
6 <sup>e</sup>		 ( <b>37</b> ) (21) +  ( <b>38</b> ) (3)	(70)
7		 ( <b>40</b> ) (27) +  ( <b>41</b> ) (23) +  ( <b>38</b> ) (24)	(14)

<sup>a</sup> Reagents and conditions: Substrates 4.0 mmol, CCl<sub>4</sub> 15 mL, temp 250 °C, time 7 h, N<sub>2</sub>.

<sup>b</sup> The yields were calculated on the basis of the peak of 1,4-dioxane using <sup>1</sup>H NMR spectroscopy.

<sup>c</sup> Time 21 h.

<sup>d</sup> Time 14 h.

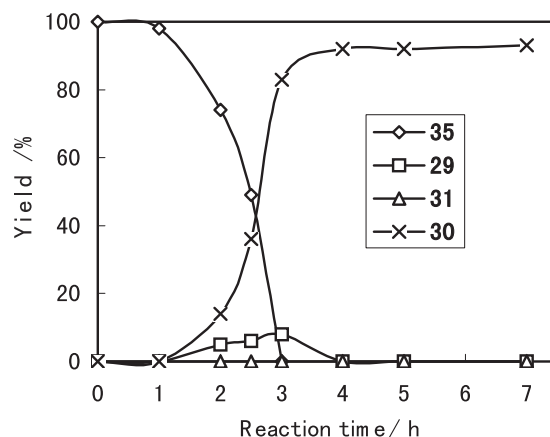
<sup>e</sup> Temp 240 °C.

**Table 4**  
Chlorination of **35** in high temperature CCl<sub>4</sub><sup>a</sup>

Entry	Time (h)	Products (Yield (%) <sup>b</sup> )			
		<b>35</b>	<b>29</b>	<b>31</b>	<b>30</b>
1	1.0	98	0	0	0
2	2.0	74	5	0	14
3	2.5	49	6	0	36
4	3.0	0	8	0	83
5	4.0	0	0	0	92
6	5.0	0	0	0	92
7	7.0	0	0	0	93

<sup>a</sup> Reagents and conditions: **35** 4.0 mmol, CCl<sub>4</sub> 15 mL, temp 250 °C, N<sub>2</sub>.

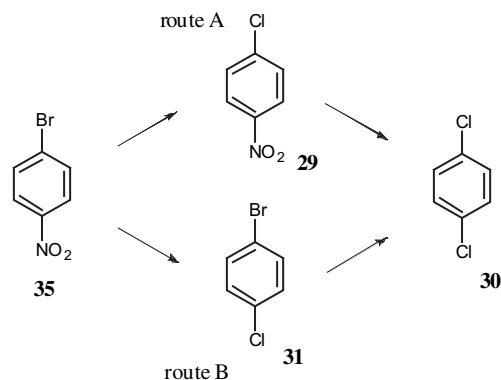
<sup>b</sup> The yields were calculated on the basis of the peak of 1,4-dioxane using <sup>1</sup>H NMR spectroscopy.



**Figure 1.** The time course of the reaction of *p*-bromonitrobenzene (**35**).

bromo groups were converted into the chloro group without the changes of the fluoro group, indicating that the fluoro group was stable under the employed conditions (entries 3 and 4).

*p*-Bromonitrobenzene (**35**) was transformed to **30** in 93% yield after 7 h (entry 5). Detailed studies were conducted for the chlorination of compound **35**. The product distributions through the progress of the reaction are summarized in Table 4 and Figure 1. The reaction pathway for the reaction of **35** is shown in Scheme 1. As shown in Scheme 1, chlorodebromination (to give **29**) and chlorodenitration (to give **31**) are competitive. Conversion of **31** into **30** is slower than that of **29** into **30** under the employed conditions (Table 3, entries 1 and 2). The starting material **35** decreased rapidly during 1–3 h, and the reactions completed after 4 h to give the final product **30** in good yield (Fig. 1). No decreasing of the substrate occurred in the initial 1 h. It may be the inductive period to generate the active species for the chlorination. During the reactions, a small amount of **29** was detected by <sup>1</sup>H NMR spectroscopy and T.L.C., indicating that transformation of **35** to **29** is faster than that of **29** to **30**. On the



**Scheme 1.** Reaction pathway of the chlorination of **35**.

other hand, compound **31** was not detected, indicating that transformation of **35** to **31** is slower than that of **31** to **30**. (Table 4). These results suggest that route A is the main process of the transformation of **35** to **30**. It was reported that small amounts of the rearrangement products, 1,2,4-trichlorobenzene and 1-chloro-2-bromo-4-nitrobenzene were produced by the photo-induced chlorination of **35** via *ipso* intermediates, and 1,2,4-trichlorobenzene was yielded by the photochemical chlorination of **29**.<sup>16,17</sup>

The displacement of the nitro and bromo groups of compounds **36** and **39** was accompanied by the chlorination at the methyl groups (Table 3, entries 6 and 7).

The transformation of other substituents on the benzene ring was investigated. The results were shown in Table 5. The reaction of benzaldehyde (**42**) gave not only benzoyl chloride (**43**) (64%) but also a small amount of chlorobenzene (**25**) (15%) (entry 1). It was reported that photochemical chlorination<sup>18</sup> and the use of sulfuryl chloride-BPO<sup>19</sup> extensively afforded benzoyl chloride **43**, while gas-phase chlorination of benzaldehyde (**42**) at 375 °C gave chlorobenzene (**25**) in a low yield (<10%) together with a large amount of carbon, probably through intermediate benzoyl and phenyl radicals.<sup>10</sup> Reactions under subcritical conditions are milder than gas-phase reactions,<sup>1</sup> so that decomposition to carbon was suppressed. Benzoyl chloride (**43**) was stable under the employed conditions, indicating that intermediacy of **43** for the conversion of benzaldehyde (**42**) into chlorobenzene (**25**) was ruled out (entry 2). The reaction of methyl benzoate (**44**) gave benzoyl chloride (**43**) (26%) and chloromethyl

**Table 5**  
The reactions of various aromatic hydrocarbons in high temperature CCl<sub>4</sub><sup>a</sup>

Entry	Substrate	Products (Yield (%) <sup>b</sup> )	Recovery (%) <sup>b</sup>
1		<b>43</b> (64) <sup>c</sup> <b>25</b> (15) <sup>c</sup>	(19)
2		N.R. <sup>d</sup>	(95)
3		<b>43</b> (26) <b>45</b> (28)	(30)
4		<b>47</b> (71)	(27)
5		<b>49</b> (54) <b>50</b> (18)	(26)
6		N.R. <sup>d</sup>	(94)
7		N.R. <sup>d</sup>	(92)

<sup>a</sup> Reagents and conditions: Substrates 4.0 mmol, CCl<sub>4</sub> 15 mL, temp 250 °C, time 7 h.

<sup>b</sup> Isolated yields.

<sup>c</sup> The yields were calculated on the basis of the peak of 1,4-dioxane using <sup>1</sup>H NMR spectroscopy.

<sup>d</sup> No reaction.

benzoate (**45**) (28%) (entry 3). Chlorination occurred at the methyl groups for the reactions of anisole and thioanisole (entries 4 and 5). Benzotrifluoride (**51**) and benzotrichloride (**52**) were inert under the employed conditions (entries 6 and 7).

The results for the chlorination of ketones were shown in Table 6. Chlorination was not observed at the methyl groups or proceeded

**Table 6**  
The reactions of ketones and 1,3-dicarbonyl compounds in high temperature CCl<sub>4</sub><sup>a</sup>

Entry	Substrate	Products (Yield (%) <sup>b</sup> )	Recovery (%) <sup>b</sup>
1		N.R. <sup>e</sup>	(76)
2		N.R. <sup>e</sup>	(89)
3		<b>56</b> (21)	(56)
4		<b>58</b> (30)	(51)
5		N.R. <sup>e</sup>	(78)
6		N.R. <sup>e</sup>	(77)
7		N.R. <sup>e</sup>	(82)
8		— <sup>f</sup>	(25)
9 <sup>c</sup> 10 <sup>d</sup>		— <sup>f</sup> N.R. <sup>e</sup>	(77) (87)
11		N.R. <sup>e</sup>	(86)
12		N.R. <sup>e</sup>	(83)

<sup>a</sup> Reagents and conditions: Substrates 4.0 mmol, CCl<sub>4</sub> 15 mL, temp 250 °C, time 7 h, N<sub>2</sub>.

<sup>b</sup> The yields were calculated on the basis of the peak of 1,4-dioxane using <sup>1</sup>H NMR spectroscopy.

<sup>c</sup> Temp 240 °C.

<sup>d</sup> Temp 230 °C.

<sup>e</sup> No reaction.

<sup>f</sup> Polymeric materials were obtained.

quite slowly at the methylene and methine groups (entries 1–4). Surprisingly, even in the cases of the 1,3-dicarbonyl compounds, which are more active than simple ketones, reactions did not occur at the activated methylene groups (entries 5–7). It has been reported that these ketones involving 1,3-dicarbonyl compounds were easily chlorinated by the traditional methods such as photo-induced chlorination<sup>20</sup> and the use of sulfonyl chloride<sup>4</sup> via the ionic mechanism. Even in the cases of more active 2-methyl-substituted-1,3-dicarbonyl compounds **62**–**64**, chlorination did not observed, although the reaction of **62** gave polymeric materials above 240 °C (entries 8–12).

Sulfones were stable under the employed conditions and most of the starting materials were recovered (entries 1–4 in Table 7). A small amount of chlorobenzene (**25**) was obtained by aromatic substitution from the reactions of sulfones **68** and **69** in 5 and 8% yields, respectively (entries 3 and 4). Benzenesulfonyl chloride and

methanesulfonyl chloride were not detected from the reactions of compounds **68** and **69**, respectively. On the other hand, benzenesulfonyl chloride (**70**) reacted smoothly to yield chlorobenzene (**25**) in 84% yield (entry 5). It was reported that chlorobenzene (**25**) was easily produced by photochemical chlorination of diphenyl sulfone (**68**) and benzenesulfonyl chloride (**70**) in quantitative yields.<sup>11,13</sup>

In contrast to the less reactivities of sulfones, sulfoxides were reduced to sulfides in a low to modest yields together with large amounts of unidentified complex (entries 6–9). Dibutyl sulfoxide (**71**), tetramethylene sulfoxide (**73**), and diphenyl sulfoxide (**75**) were converted into the corresponding sulfides **72**, **74**, and **76** in 61, 24, and 59% yields, respectively (entries 6–8). Chloromethyl phenyl sulfide (**49**) and dichloromethyl phenyl sulfide (**50**) were isolated from the reaction of sulfoxide **77** in 15 and 11% yields, respectively (entry 9). Reduction of sulfoxides to sulfides with Br<sub>2</sub>–HBr system has been reported by Oae, although diphenyl sulfoxide **75** was recovered quantitatively.<sup>21</sup>

As for the chlorination of alkyl groups adjacent to the functional groups listed in Tables 5–7, the reactions proceeded more easily for anisole and thioanisole, which possess electron-donative oxygen and sulfur atoms, respectively (Table 5, entries 4 and 5). On the other hand, the reactions were quite slow for ketones and sulfones, which have electron-withdrawing carbonyl and sulfonyl groups (Table 6, entries 1–7, 11, and 12, and Table 7, entries 1, 2, and 4).

Finally, the reactions of olefins were explored. The results are summarized in Table 8. Interestingly, the coupling adducts **79**, **81**, and **83** between olefins and carbon tetrachloride were obtained (entries 1–3), although the yield of compound **81** was low (12%) because of the production of unidentified complex mixtures. The observed regioselectivities show that the trichloromethyl radical was introduced into olefins first. Compounds **81**<sup>22</sup> and **83** were obtained as a mixture (1:1) and (2:1) of *anti/syn* isomers, respectively (entries 2 and 3). The starting material was recovered quantitatively in the case of stilbene (**84**) (entry 4). Because of the steric hindrance between the trichloromethyl radical and the phenyl group on stilbene, the formation of the coupling adduct might be restricted. It was reported that photo-induced chlorination<sup>3</sup> and the use of sulfonyl chloride–BPO<sup>4</sup> resulted in the addition of Cl<sub>2</sub> to the olefinic double bond via radical mechanisms. The BPO-induced addition of sulfonyl chloride to 1-alkenes, which affords β-chloro-*n*-alkyl sulfones has been reported by Kharasch and Zavist.<sup>23</sup>

**Table 7**  
The reactions of sulfones and sulfoxides in high temperature CCl<sub>4</sub><sup>a</sup>

Entry	Substrate	Products (Yield (%) <sup>b</sup> )	Recovery (%) <sup>b</sup>
1	<b>65</b>	<b>66</b> (3)	(87)
2	<b>67</b>	N.R. <sup>e</sup>	(92)
3	<b>68</b>	<b>25</b> (5) <sup>f</sup>	(94)
4	<b>69</b>	<b>25</b> (8) <sup>f</sup>	(87)
5	<b>70</b>	<b>25</b> (84) <sup>f</sup>	(9)
6 <sup>c</sup>	<b>71</b>	<b>72</b> (61) <sup>f,g</sup>	(0)
7 <sup>d</sup>	<b>73</b>	<b>74</b> (24) <sup>f,g</sup>	(0)
8	<b>75</b>	<b>76</b> (59) <sup>g</sup>	(0)
9	<b>77</b>	<b>49</b> (15) <sup>g</sup> <b>50</b> (11) <sup>g</sup>	(0)

<sup>a</sup> Reagents and conditions: Substrates 4.0 mmol, CCl<sub>4</sub>, 15 mL, temp 250 °C, time 7 h, N<sub>2</sub>.

<sup>b</sup> Isolated yields.

<sup>c</sup> Temp 220 °C.

<sup>d</sup> Temp 200 °C.

<sup>e</sup> No reaction.

<sup>f</sup> The yields were calculated on the basis of the peak of 1,4-dioxane using <sup>1</sup>H NMR spectroscopy.

<sup>g</sup> Complex mixture was obtained.

**Table 8**  
The reactions of various olefins in high temperature CCl<sub>4</sub><sup>a</sup>

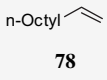
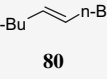
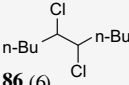
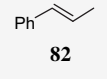
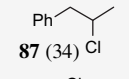
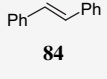
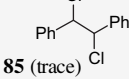
Entry	Substrate	Time(h)	Products (Yield (%) <sup>b</sup> )	Recovery (%) <sup>b</sup>
1	<b>78</b>	8	<b>79</b> (81) CCl <sub>3</sub>	(0)
2	<b>80</b>	7	<b>81</b> (12) <sup>c</sup> CCl <sub>3</sub>	(21)
3	<b>82</b>	7	<b>83</b> (74) CCl <sub>3</sub>	(5)
4	<b>84</b>	8	<b>85</b> (2) Cl	(98)

<sup>a</sup> Reagents and conditions: Substrates 4.0 mmol, CCl<sub>4</sub> 15 mL, temp 250 °C, N<sub>2</sub>.

<sup>b</sup> Isolated yields.

<sup>c</sup> Complex mixture was obtained.

**Table 9**  
The reactions of various olefins in high temperature  $\text{CHCl}_3^a$

Entry	Substrate	Time (h)	Products (Yield (%) <sup>b</sup> )	Recovery (%) <sup>b</sup>
1	 <b>78</b>	7	— <sup>c</sup>	(62)
2	 <b>80</b>	7	 <b>86</b> (6)	(81)
3	 <b>82</b>	7	 <b>87</b> (34)	(34)
4	 <b>84</b>	7	 <b>85</b> (trace)	(99)

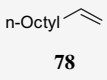
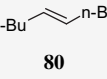
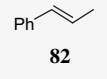
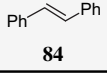
<sup>a</sup> Reagents and conditions: Substrates 4.0 mmol,  $\text{CCl}_4$  15 mL, temp 250 °C,  $\text{N}_2$ .

<sup>b</sup> Isolated yields.

<sup>c</sup> Complex mixture was obtained.

The results of the reactions of olefins **78**, **80**, **82**, and **84** in subcritical chloroform were summarized in Table 9. The reactions in subcritical chloroform proceeded more slowly than in carbon tetrachloride, and the reactions gave different results depending on the structure of olefins. The reaction of compound **78** gave only unidentified complex mixture (entry 1). Most of the starting materials were recovered in the cases of **80** and **84** (entries 2 and 4). The adduct **87** between the olefin and HCl was obtained by the chlorination of **82** (entry 3). The results for the chlorination of olefins **78**, **80**, **82**, and **84** in subcritical dichloromethane were shown in Table 10. These olefins were stable under the employed conditions except **78**, which was transformed to unidentified complex mixture.

**Table 10**  
The reactions of various olefins in high temperature  $\text{CH}_2\text{Cl}_2^a$

Entry	Substrate	Time (h)	Products (Yield (%) <sup>b</sup> )	Recovery (%) <sup>b</sup>
1	 <b>78</b>	7	— <sup>c</sup>	(63)
2	 <b>80</b>	7	N.R. <sup>d</sup>	(83)
3	 <b>82</b>	7	N.R. <sup>d</sup>	(93)
4	 <b>84</b>	7	N.R. <sup>d</sup>	(93)

<sup>a</sup> Reagents and conditions: Substrates 4.0 mmol,  $\text{CCl}_4$  15 mL, temp 250 °C,  $\text{N}_2$ .

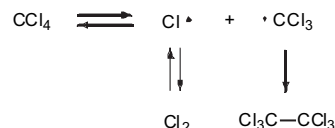
<sup>b</sup> Isolated yields.

<sup>c</sup> Complex mixture was obtained.

<sup>d</sup> No reaction.

During the reactions, a large amount of  $\text{Cl}_2$  was evolved, which was detected by DPD (diethyl-*p*-phenylenediamine) and syringaldazine (3,5-dimethoxy-4-hydroxybenzalazine) methods. The plausible mechanism for the formation of  $\text{Cl}_2$  was shown in Scheme 2. Thermal cleavage of the C–Cl bond of carbon tetrachloride would afford the chloro radical and the trichloromethyl radical. Coupling of the chloro radical gives  $\text{Cl}_2$ . Dimerization of the trichloromethyl radical probably leads to hexachloroethane.<sup>24</sup> Hexachloroethane was detected by GC–MS spectroscopy in the reaction of carbon tetrachloride at 250 °C for 7 h. The resulting chloro radical would react with the aliphatic and aromatic substrates to give the chlorinated

products via the free-radical chain mechanism, while the addition of chloro and trichloromethyl radicals to olefins leads to the coupling adducts. Chloroform, which was generated by the abstraction of the hydrogen atom of the trichloromethyl radical from the substrate, was detected by GC–MS spectroscopy in the chlorination of adamantane. In spite of the considerable stability of carbon tetrachloride at higher temperature (ca. 500 °C),<sup>25</sup> the cleavage of the C–Cl bond occurred more easily under subcritical conditions. The methods to generate the trichloromethyl radical via the cleavage of carbon tetrachloride promoted by  $\text{Fe}^{26}$  and ruthenium complexes<sup>27</sup> have been reported.



**Scheme 2.** Mechanism of the decomposition of  $\text{CCl}_4$ .

### 3. Conclusions

In conclusion, we carried out the chlorination of aliphatic hydrocarbons and side chains of aromatic hydrocarbons in subcritical carbon tetrachloride. In addition, the reactions of a variety of aromatic compounds including 1,4-disubstituted benzenes were examined. The rearranged products were not detected from the reactions of 1,4-disubstituted benzenes. Interestingly, strongly radicalic atmosphere was formed for the chlorination of benzaldehyde, ketones, and sulfones. The addition of carbon tetrachloride to olefins is the characteristic reaction under high temperature conditions.

### 4. Experimental

#### 4.1. General methods

IR spectra were recorded on a Hitachi I-3000 spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Varian plus-500 W or a Hitachi R-1200 spectrometer using tetramethylsilane as an internal standard. Column chromatography was performed on Wakogel C-200. The Teflon-lined stainless autoclave was purchased from OM Lab-Tech Co. Ltd., Japan. Carbon tetrachloride was refluxed with  $\text{P}_2\text{O}_5$  and distilled prior to use. Compounds **41**,<sup>29</sup> **47**,<sup>30</sup> **66**,<sup>31</sup> and **86**<sup>23</sup> were identified by comparison of their spectroscopic behaviors with those of authentic samples. All products obtained in this study otherwise mentioned were completely characterized by comparison with commercially available samples. Hexachloroethane and chloroform in the reaction mixture were identified by comparison of their GC–MS spectra with those of commercially available samples. Detection of  $\text{Cl}_2$  was carried out by the ION SELECTIVE PACK TEST kit, WAK-CIO/DP (Kyoritsu Chemical-Check Lab. Corp.), which DPD (diethyl-*p*-phenylenediamine) was employed as a detection agent, or the test paper, Nissan Aqua Check LC, which syringaldazine (3,5-dimethoxy-4-hydroxybenzalazine) was applied (purchased from AS ONE Co.).

#### 4.2. A typical experimental procedure

A mixture of adamantane (**1**) (4.0 mmol) and carbon tetrachloride (15 mL) in a 28 mL Teflon-lined stainless autoclave was heated at 250 °C under nitrogen. The internal pressure reached ca. 7 MPa. The mixture was heated at the same temperature for 4 h. After cooling, the solution was washed with water, dried and evaporated. The residue was chromatographed (hexane) on silica gel to give **2**, **3**, and **4** in 52, 9, and 3% yields, respectively. Compound **1** was recovered in 15% (Table 1, entry 1).

**Caution!** Attention should be paid for the leak of the gas since a large amount of harmful chlorine was evolved during the

reactions. It is important to firmly tighten the screw of the stainless autoclave. The operation should be carried out in a well-ventilated fume hood when the autoclave was opened. Many times use of the stainless autoclave should be avoided because of the rust caused by chlorine gas. The authors recommend these reactions not for synthetic methods of chlorination, but for investigations of subcritical chemistry because this method is dangerous.

**4.2.1. Isolation of triphenylmethyl chloride (17).** A mixture of triphenylmethane (**16**) (4.0 mmol) and carbon tetrachloride (15 mL) in a 28 mL Teflon-lined stainless autoclave was heated at 250 °C for 7 h under nitrogen. After cooling, the solution was evaporated at room temperature under reduced pressure to give triphenylmethyl chloride **17** in 99% yield. (Table 1, entry 10). Colorless solid, mp 111–112 °C (benzene) (lit.,<sup>28</sup> 111–112 °C). Chloride **17** was converted into triphenylmethanol quantitatively by the treatment of carbon tetrachloride with water or column chromatography on silica gel.

**4.2.2. 1-(4-Chloromethylphenyl)adamantane (22).** Colorless needles, mp 92–94 °C (from acetone); IR (KBr)  $\nu_{\max}$  3440, 2920, 2856, 1518, 1452, 1384, 1344, 1332, 1320, 1310, 1286, 1118, 1104, 1032, 1016, 968, 864, 840, 800, 724, 534  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.70–2.35 (15H, m, CH, and  $\text{CH}_2$ ), 4.50 (2H, s,  $\text{CH}_2\text{Cl}$ ), 7.35 (2H, d,  $J=8.7$  Hz, ArH), 7.38 (2H, d,  $J=8.7$  Hz, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  28.9 (d), 36.1 (s), 36.7 (t), 43.1 (t), 46.2 (t), 125.3 (d), 128.4 (d), 134.5 (s), 151.7 (s). Anal. Calcd for  $\text{C}_{17}\text{H}_{21}\text{Cl}$ : C, 78.29; H, 8.12. Found: C, 78.41; H, 8.10.

**4.2.3. 1-Chloro-3-p-tolyladamantane (23).** Colorless needles, mp 69–71 °C (from acetone); IR (KBr)  $\nu_{\max}$  3448, 2908, 2848, 1614, 1516, 1448, 1414, 1342, 1272, 1102, 1034, 1018, 976, 842, 832, 804, 744, 692, 672, 536  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.54–2.28 (14H, m, CH, and  $\text{CH}_2$ ), 2.32 (3H, s,  $\text{CH}_3$ ), 7.14 (2H, d,  $J=8.9$  Hz, ArH), 7.23 (2H, d,  $J=8.9$  Hz, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  20.9 (q), 31.9 (d), 34.7 (t), 40.2 (s), 41.4 (t), 46.9 (t), 52.8 (t), 68.8 (s), 124.6 (d), 129.0 (d), 135.5 (s), 145.9 (s). Anal. Calcd for  $\text{C}_{17}\text{H}_{21}\text{Cl}$ : C, 78.29; H, 8.12. Found: C, 78.31; H, 8.08.

**4.2.4. 1,1,1,3-Tetrachloroundecane (79).** Colorless oil; IR (neat)  $\nu_{\max}$  2932, 1860, 1468, 1380, 1210, 1124, 1050, 962, 788, 701, 574  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.89 (3H, t,  $J=6.6$  Hz,  $\text{CH}_3$ ), 1.10–1.70 (12H, m,  $\text{CH}_2$ ), 1.70–2.18 (2H, m,  $\text{CH}_2$ ), 3.04 (1H, dd,  $J=15.0$  and 4.8 Hz,  $\text{CHCl}_3$ ), 3.33 (1H, dd,  $J=15.8$  and 5.1 Hz,  $\text{CHCl}_3$ ), 4.08–4.48 (1H, m,  $\text{CHCl}$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  14.1 (q), 22.7 (t), 26.0 (t), 28.9 (t), 29.2 (t), 29.3 (t), 31.8 (t), 39.1 (t), 57.7 (d), 62.3 (t), 97.0 (s). Anal. Calcd for  $\text{C}_{11}\text{H}_{20}\text{Cl}_4$ : C, 44.92; H, 6.85. Found: C, 44.83; H, 7.00.

**4.2.5. 5-Chloro-6-trichloromethyldecane (81)<sup>17</sup>.** Compound **81** was obtained as a mixture (1:1) of *anti/syn* isomers. Colorless oil; IR (neat)  $\nu_{\max}$  2959, 2872, 1465, 1380, 987, 907, 984, 635  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.93 (6H, t,  $J=6.6$  Hz,  $\text{CH}_3$ ), 1.20–2.30 (12H, m,  $\text{CH}_2$ ), 2.55 (1H<sub>syn</sub>, td,  $J=4.6$  and 1.0 Hz,  $\text{CHCl}_3$ ), 2.90–3.15 (1H<sub>anti</sub>, m,  $\text{CHCl}_3$ ), 4.64 (1H, td,  $J=6.3$  and 1.6 Hz,  $\text{CHCl}$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  13.8 (q), 13.9 (q), 22.0 (t), 22.9 (t), 27.5 (*C<sub>anti</sub>*, t), 28.5 (*C<sub>syn</sub>*, t), 29.0 (*C<sub>syn</sub>*, t), 29.4 (*C<sub>anti</sub>*, t), 31.8 (*C<sub>anti</sub>*, t), 32.2 (*C<sub>syn</sub>*, t), 32.7 (*C<sub>anti</sub>*, t), 39.0 (*C<sub>syn</sub>*, t), 62.4 (*C<sub>syn</sub>*, d), 62.7 (*C<sub>anti</sub>*, d), 63.3 (*C<sub>syn</sub>*, d), 65.4 (*C<sub>anti</sub>*, d), 103.1 (*C<sub>anti</sub>*, s), 104.1 (*C<sub>syn</sub>*, s). Anal. Calcd for  $\text{C}_{11}\text{H}_{20}\text{Cl}_4$ : C, 44.92; H, 6.85. Found: C, 44.64; H, 6.74.

**4.2.6. 1,3,3,3-Tetrachloro-2-methylpropylbenzene (83).** Compound **83** was obtained as a mixture (2:1) of *anti/syn* isomers. Colorless oil; IR (neat)  $\nu_{\max}$  3063, 3031, 2998, 2947, 1602, 1495, 1453, 1382, 1309, 1232, 1122, 1076, 1043, 950, 917, 856, 825, 768, 699, 639, 570  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.47 (3H<sub>syn</sub>, t,  $J=6.8$  Hz,  $\text{CH}_3$ ), 1.50 (3H<sub>anti</sub>, t,  $J=6.6$  Hz,  $\text{CH}_3$ ), 2.99 (1H<sub>anti</sub>, qd,  $J=6.4$  and 1.4 Hz,  $\text{CHCl}_3$ ), 3.17–3.50 (1H<sub>syn</sub>, m,  $\text{CHCl}_3$ ), 5.77 (1H<sub>syn</sub>, d,  $J=3.6$  Hz,  $\text{CHCl}$ ), 5.81 (1H<sub>anti</sub>, d,  $J=1.6$  Hz,  $\text{CHCl}$ ), 7.17 (5H, m, ArH);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  11.4 (*C<sub>anti</sub>*, q), 12.2 (*C<sub>syn</sub>*, q), 60.8 (*C<sub>anti</sub>*, d), 61.2 (*C<sub>syn</sub>*, d), 61.9 (*C<sub>syn</sub>*, d), 62.1 (*C<sub>anti</sub>*, d),

103.2 (s), 126.8 (*C<sub>anti</sub>*, d), 127.9 (*C<sub>syn</sub>*, d), 128.2 (*C<sub>anti</sub>*, d), 128.6 (*C<sub>anti</sub>*, d), 128.7 (*C<sub>syn</sub>*, d), 129.3 (*C<sub>syn</sub>*, d), 136.7 (*C<sub>syn</sub>*, s), 140.6 (*C<sub>anti</sub>*, s). Anal. Calcd for  $\text{C}_{10}\text{H}_{10}\text{Cl}_4$ : C, 44.16; H, 3.71. Found: C, 44.40; H, 3.73.

### 4.3. A typical experimental procedure for the determination of the yields by $^1\text{H NMR}$ spectroscopy

A mixture of toluene (**12**) (4.0 mmol) and carbon tetrachloride (15 mL) in a 28 mL Teflon-lined stainless autoclave was heated at 250 °C for 7 h under nitrogen. After cooling, the yield of benzyl chloride (**13**) was calculated on the basis of the peak of 1,4-dioxane using  $^1\text{H NMR}$  spectroscopy (Table 1, entry 8).

### 4.4. Determination of the yields of the products for the chlorination of 35

A mixture of toluene (**35**) (4.0 mmol) and carbon tetrachloride (15 mL) in a 28 mL Teflon-lined stainless autoclave was heated at 250 °C under nitrogen. After 1.0, 2.0, 2.5, 3.0, 4.0, 5.0, and 7.0 h, the autoclave was cooled and the yields of the products were calculated on the basis of the peak of 1,4-dioxane using  $^1\text{H NMR}$  spectroscopy (Table 4).

### Acknowledgements

We thank Nitto Analytical Techno Center for the analyses of GC–MS. We thank the Research Promotion Grant (NDUF-08-15) from Nippon Dental University.

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