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Transformation of Ketones into 1-Chloro and 1,1-Dichloro-1-alkenes by Means of a Polychloromethane-Titanocene(II) System

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Abstract: The olefination of ketones using the organotitanium species formed from $Cp_2Ti[P(OEt)_3]_2$ and polychloromethane was studied. The reaction of the organotitanium species prepared from carbon tetrachloride with ketones produced the 1,1-dichloro-1-alkenes in good yields even when dialkyl ketones were employed. The similar olefination of ketones using chloroform afforded the 1-chloro-1-alkenes and 1,1-dichloro-1-alkenes, the ratio of which reflected the steric demand on the ketones. The titanocene chloromethylidene complex was suggested to be an active species of the reaction on the basis of the results obtained by the reaction using chloroform-*d*.

INTRODUCTION

Carbonyl olefination is one of the most fundamental transformations in organic synthesis, and various types of unsaturated compounds are prepared by this process. For the conversion of carbonyl compounds to 1,1-dihaloalkenes, the Wittig type reaction using dihalomethylenephosphorane is frequently employed.[1] Although these reactions effect the transformation of aldehydes, aromatic ketones, and certain cyclic ketones to the corresponding 1,1-dihaloalkenes, attempts to prepare such compounds from dialkyl ketones are generally unsuccessful. For example, the reaction of dibromomethylenetriphenylphosphorane generated *in situ* from carbon tetrabromide and triphenylphosphine with 2-octanone affords the dibromoolefin in low yield, and 5-nonanone is unreactive towards the phosphorane.[1i] One successful procedure for the conversion of ketones to 1,1-dichloro-1-alkene utilizes lithium salt of diethyl dichloromethanephosphonate.[2] Although cyclic ketones and certain methyl ketones are transformed into the dichlorides by this reaction, the preparation of the requisite reagent is rather complicated. The Peterson olefination using (trimethylsilyl)dichloromethyllithium was employed for the dichloromethylenation of aldehydes,[3] however its application to ketones has not yet been reported.

Recently we disclosed an efficient method for the olefination of carbonyl compounds using a *gem*-dichlorides-$Cp_2Ti[P(OEt)_3]_2$ system.[4] Unlike conventional olefination reactions, this procedure is extremely effective for the preparation of highly substituted olefins and enol ethers. These results prompted us to study the transformation of ketones **1** to haloolefins using the organotitanium reagent prepared from polyhalomethanes **2** and the low-valent titanium species $Cp_2Ti[P(OEt)_3]_2$ **3**. In this paper we describe the preparation of 1,1-di-

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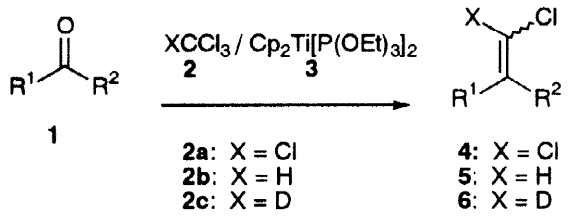
chloro- and 1-chloro-1-alkenes **4** and **5** using carbon tetrachloride (**2a**) and chloroform (**2b**) as sources of the olefination reagents (Scheme 1). The reaction mechanism is also discussed based on the results of the olefination using chloroform-*d* (**2c**).



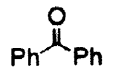
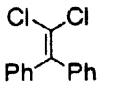
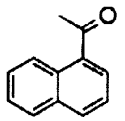
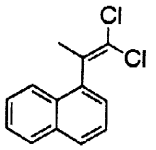
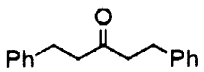
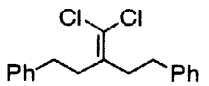
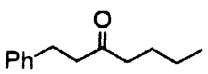
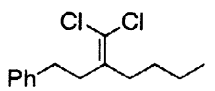
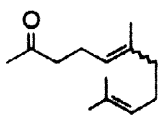
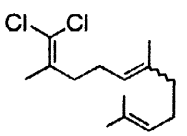
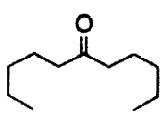
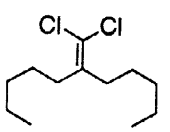
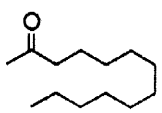
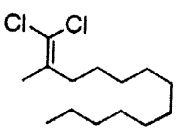
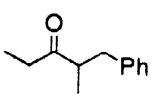
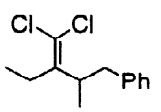
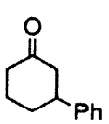
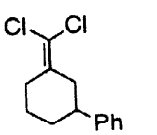
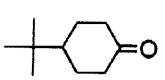
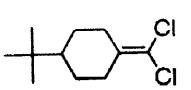
Scheme 1

RESULTS AND DISCUSSION

Carbon tetrachloride (**2a**) (2 equiv) was reduced with the low-valent titanium **3** (6 equiv), prepared by the reduction of Cp_2TiCl_2 with magnesium turnings in the presence of $P(OEt)_3$ and powdered molecular sieves 4A, at room temperature for 10 min. The treatment of the resulting organotitanium species with 1,5-diphenyl-3-pentanone (**1c**) produced dichloroolefin **4c** in 59% yield (Scheme 1). When the preparation and reaction of organotitanium reagent were carried out at 0 °C, the yield was slightly increased to 63% and a small amount (16%) of the starting ketone was recovered (Table 1, entry 3). Although all the starting ketone was consumed when large excess of carbon tetrachloride and **3** were employed, the olefination product **4c** was obtained in comparable yield. Similar treatment of carbon tetrabromide with the low-valent titanium **3** and **1c** afforded no olefination product, and the starting ketone was recovered (85%). Under the optimized reaction conditions, the reactions of various ketones were performed. As the results in Table 1 indicate, 1,1-dichloro-1-alkenes **4** were obtained in good yields even when dialkyl ketones were employed. However, the olefination of benzophenone (**1a**) was exceptional and gave dichloroolefin **4a** only in 22% yield though the Wittig type reaction is effective for the transformation of aromatic ketones.[1c] The transformation of sterically hindered α-substituted dialkyl ketone **1h** also afforded the dichloromethylidene derivative **4h** in low yield (20%), and a considerable amount of the starting ketone was recovered (49%) (entry 8). It was found that **4** was contaminated with a trace amount of 1-chloro-1-alkene **5** in cases of **1a** and **c** (entries 1 and 3). The formation of **5** is explained by the reduction of **4** with magnesium remained in the reaction mixture.

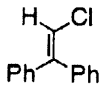
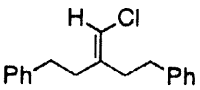
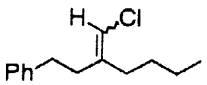
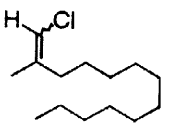
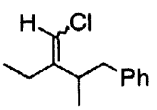
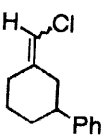
Further we studied the transformation of ketones into vinyl chlorides using chloroform (**2b**). We initially used technical grade **2b** (99.5+% purity) after purification by passage through a column of alumina just prior to use. The reaction of **1c** using 6 equiv of **3** and 2 equiv of **2b** at 0 °C produced the vinyl chloride **5b** in 39% yield along with a small amount of the 1,1-dichloro-1-alkene **4c**. The yield of **5b** increased (63%) with increasing the molar ratio of **2b** (3 equiv). Furthermore we found that the yield was influenced by the purity of chloroform used; **5b** was obtained in better yield (70%) when highly pure **2b** (3 equiv) (99.9+%, Aldrich) was employed (Table 2, entry 2). The concomitant formation of 1,1-dichloro-1-alkene **4** was observed in most of

Table 1. Olefination of Ketones **1** with Carbon Tetrachloride **2a**

Entry	Ketone **1**		Time / h	Product **4**		Yield / %
1		**1a**	19		**4a**	22[a]
2		**1b**	20		**4b**	66
3		**1c**	3		**4c**	64[a]
4		**1d**	2		**4d**	62
5		**1e**[b]	2		**4e**[c]	72
6		**1f**	2		**4f**	58
7		**1g**	1.5		**4g**	74
8		**1h**	19		**4h**	20
9		**1i**	21		**4i**	61
10		**1j**	2		**4j**	58

a) Contaminated with a trace amount (< 1%) of the chloromethylenation product **5**. b) $E : Z = 60 : 40$. c) The ratio of stereoisomers was not determined.

Table 2. Olefination of Ketones **1** with Chloroform **2b**.

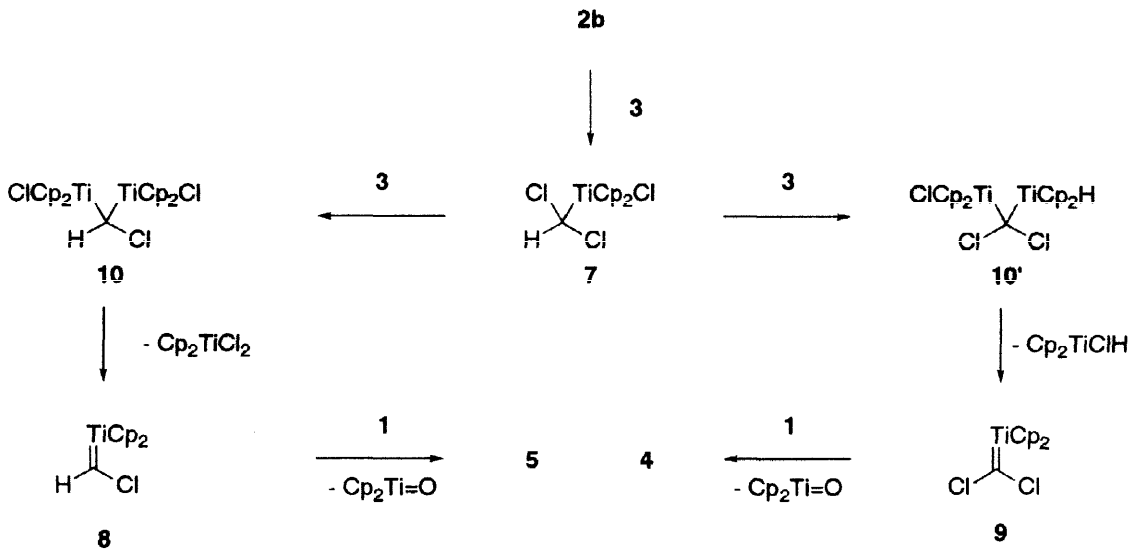
Entry	Ketone **1**	Time / h	Product (Yield / %; Ratio of stereoisomers)[a]		
1	**1a**	16		**5a** (89)	
2	**1c**	18		**5b** (70)	**4c** (18)
3	**1d**	2.5		**5c** (83; 51 : 49)	**4d** (15)
4[b]	**1g**	2.5		**5d** (53; 62 : 38)	**4g** (39)
5	**1h**	19		**5e** (56; 93 : 7)	
6	**1i**	19		**5f** (60; 51 : 49)	**4i** (22)

a) Determined by NMR spectroscopy. b) **5d** and **4g** were obtained as a mixture. The yields were determined by NMR analysis.

the cases examined (Table 2). The proportion of monochloroolefin **5** and dichloroolefin **4** in this reaction seems to be dependent on the steric hindrance of ketone to the approaching organotitanium species.

In contrast to the dichloroolefination using carbon tetrachloride **2a**, the monochloroolefin **5a** was produced selectively in high yield by the reaction of **1a** with chloroform **2b** (entry 1). The reaction of sterically hindered α-substituted dialkyl ketone **1h** also gave the chloroolefin **5e** in good yield without formation of the corresponding dichloride (entry 5). Similarly the reactions of dialkyl ketones **1c** and **d** afforded **5b** and **c** with better selectivity than that of the reactions of methyl ketone **1g** and cyclic ketone **1i**. These results indicate that the two organotitanium species would be formed by the treatment of chloroform with $Cp_2Ti[P(OEt)_3]_2$ **3**, and these intermediates react with ketones to produce monochlorides **5** and dichlorides **4**, respectively. We have reported the carbonyl olefination using thioacetals and the low-valent titanium species **3**.[5] We proposed the titanium-carbene complex as an intermediate of this reaction on the basis of the results of its reactions with organic molecules having a carbon-carbon multiple bond[6] and group 14 metal hydrides.[7] It is reasonable to as-

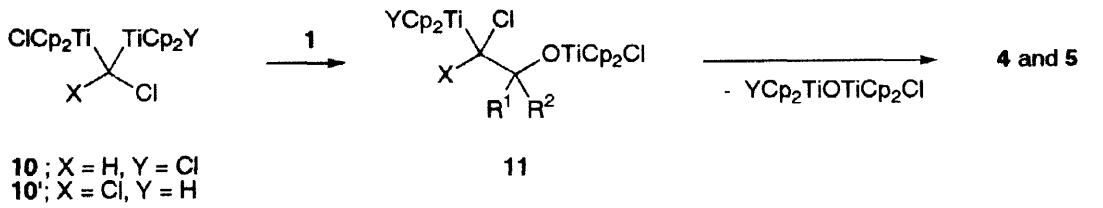
sume that the present reaction also proceeds through the formation of similar titanium-carbene intermediates as outlined in Scheme 2. The first step of the reaction is the oxidative addition of chloroform to the low-valent titanium **3** to form the alkyltitanium compound **7**. The two types of titanium-carbene complexes **8** and **9** are produced by the further reaction of **7** with **3**, in which both C-Cl and C-H bonds are cleaved. It is obvious that the reaction of dichloromethylidene complex **9** with ketones is largely affected by steric hindrance, compared with that of chloromethylene complex **8**. Considering that a large excess of **3** (6 equiv) and **2b** (3 equiv) were used, the observed variable proportions of **5** and **4** depending on the substituents of ketones is explicable by the difference of reactivity between **8** and **9**.



Scheme 2

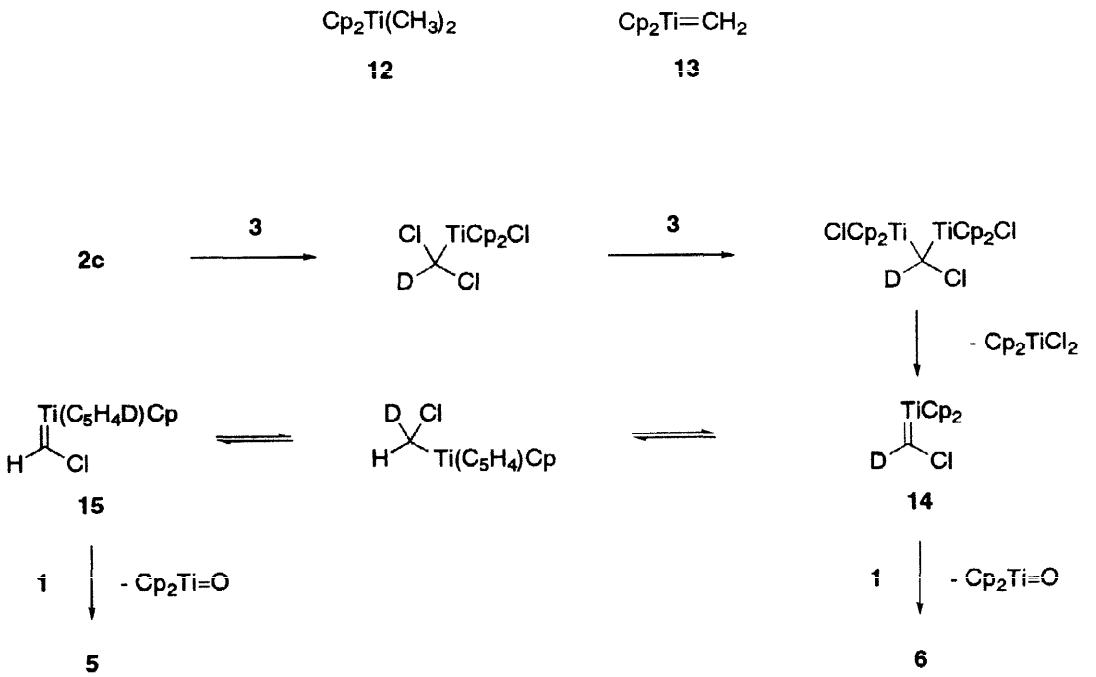
Several methods for the transformation of carbonyl compounds into 1-chloro-1-alkenes with one carbon homologation have been reported. The reagent prepared from haloform and chromium(II) chloride has been employed for the stereoselective transformation of aldehydes to 1-haloolefins.[8] The most frequently employed method for the preparation of chloroolefins from carbonyl compounds is the Wittig-type reaction using chloromethylenetriphenylphosphorane.[9] Similarly to the other carbonyl olefinations, this Wittig-type reaction is largely affected by steric hindrance, and the yields tend to be decreased when dialkyl ketones are subjected to the reaction.[1b] It should be noted that the present chloroolefination is a good alternative synthetic method especially for the transformation of dialkyl ketones.

We have further investigated the pathway of this reaction using chloroform-*d* (**2c**) as a source of the organotitanium species. As stated above, we tentatively assume that the low-valent titanium **3** promoted chloroolefination proceeds through the formation of carbene complexes. However the observation that both mono- and dichloroolefins are produced by the olefination using chloroform do not exclude the pathway depicted in Scheme 3, in which the *gem*-dititanium species **10** and **10'** react with a ketone **1** to produce the adducts such as **11**. A similar *gem*-dichromium compound has been suggested as an active species of the haloolefination using a haloform-chromium(II) chloride system.[8]



Scheme 3

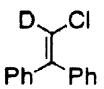
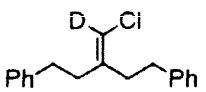
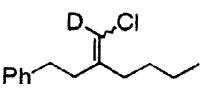
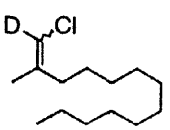
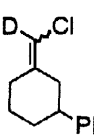
McCowan and his coworkers have studied the thermal decomposition of dimethyltitanocene **12** and its deuteriated analogue.[10] The thermolysis of **12** was reported to proceed through the formation of titanocene methylidene complex **13**. The subsequent thermal decomposition of **13** leads to produce certain titanium compounds and methane. On the basis of the observation that the Cp ring hydrogens were incorporated into methane, they proposed that a species equivalent to $Cp(C_5H_4)TiMe$ is formed from **13** by the reversible hydrogen abstraction from a Cp ring. If the chloroolefination of ketones with chloroform-*d* **2c** would take place via the formation of the deuteriated chloromethylidene complex **14**, one would expect that the H/D scrambling between the hydrogens of Cp ring and chloromethylidene group proceeds to produce the new carbene complex **15** which then reacts with a ketone to afford the undeuterated olefin **5** as a byproduct (Scheme 4).



Scheme 4

When we examined the reactions of chloroform-*d* **2c** (purity 99.8%) with ketones, we observed the formation of the deuteriated chloroolefins **6** along with the olefins possessing no deuterium **5** (Table 3). These results suggest that the present reaction proceed through the formation of titanium carbene complex. Although the dichlorides **4** were produced, the relative ratio of dichloride / monochloride was smaller than that observed in the reactions using chloroform **2b**. This may be due to the deuterium isotope effect on the formation of dichloromethylidene complex **9** by the oxidative addition of **7** to the low-valent titanium **3**. It should be noted that the present reaction provides a straightforward route to 1-chloro-1-deuterio-1-alkenes.

Table 3. Olefination of Ketones **1** with Chloroform-*d* **2c**.[a]

Entry	Ketone **1**	Time / h	Product (Yield / %; Ratio of stereoisomers)[b]		
1	**1a**	18		**6a** (70)	**5a** (8)
2	**1c**	18		**6b** (63)	**5b** (6)
3	**1d**	6		**6c** (57; 51 : 49)	**5c** (6; 53 : 47) **4d** (9)
4	**1g**	19		**6d** (52; 62 : 38)	**5d** (8; 62 : 38) **4g** (17)
5	**1i**	20		**6e** (56; 52 : 48)	**5f** (5; 52 : 48) **4i** (13)

a) The products were obtained as a mixture. b) Determined by NMR spectroscopy.

CONCLUSION

We have established new methods for the chloro- and dichloromethylenation of ketones which are especially useful for the transformation of dialkyl ketones. The fact that the chloromethylenation using chloroform-*d* produces a significant amount of the undeuterated olefin suggests that the intermediates of the present reactions would be the titanium-carbene complexes.

EXPERIMENTAL SECTION

General. All the reactions were carried out in a dry reaction vessel under argon. All melting points were determined with a Yanaco MP-S3 micromelting point apparatus. ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were measured in $CDCl_3$ on Jeol ALPHA-500 instrument and are reported in parts per million from tetramethylsilane. IR spectra were recorded on a Jeol Diamond-20 FT-IR spectrometer; absorptions are reported in cm^{-1}. Elemental analyses were performed by Perkin Elmer 2400II.

Materials. For preparative thin layer chromatography (PTLC), Wakogel B-5F was used as an adsorbent. THF was distilled from sodium and benzophenone. Magnesium turnings were purchased from Nakarai Tesque Inc. (Kyoto, Japan).

Reaction of 1,5-diphenylpentan-3-one (1c) with carbon tetrachloride (2a). Finely powdered molecular sieves 4A (300 mg), magnesium turnings (73 mg, 3 mmol), and Cp_2TiCl_2 (747 mg, 3 mmol) were placed in a flask and dried by heating with a heat gun under reduced pressure (2 mmHg). Care was taken not to sublimate Cp_2TiCl_2. After cooling, THF (4 mL) and $P(OEt)_3$ (1.06 mL, 6 mmol) were added successively with stirring at room temperature under argon. Within 15 min, the reaction mixture turned dark green and then dark brown with slight evolution of heat. After 3 h, the flask was immersed in an ice bath and stirring was continued for 20 min. Carbon tetrachloride (**2a**) (0.15 mL, 1.5 mmol) was added dropwise and the reaction mixture was stirred for 10 min. Then a THF (2 mL) solution of **1c** (119 mg, 0.5 mmol) was added dropwise. After being stirred for 3 h, the reaction mixture was diluted with hexane (30 mL) and the insoluble materials were filtered off through celite. The filtrate was condensed under reduced pressure. The crude product was purified by PTLC (hexane) to yield 98 mg (64%) of 1,1-dichloro-4-phenyl-2-phenethylbut-1-ene (**4c**).

The Physical Properties of 1,1-dichloro-1-alkenes 4. 1,1-Dichloro-2,2-diphenylethene (4a) (Entry 1, Table 1). mp 79-80.5 °C (lit.[1c] mp 80-81 °C); ^1H NMR δ 7.26-7.37 (m, 10H); ^{13}C NMR δ 119.50, 127.97, 128.25, 129.24, 139.47, 140.47; IR (KBr) 3086, 3064, 3033, 1601, 1576, 1567, 1496, 1444, 970, 858, 698, 644, 613 cm^{-1}.

1-(2,2-Dichloro-1-methylethenyl)naphthalene (4b) (Entry 2, Table 1). mp 51-52 °C; ^1H NMR δ 2.28 (s, 3H), 7.28 (dd, J= 7.0, 0.9 Hz, 1H), 7.44-7.54 (m, 3H), 7.72-7.90 (m, 3H); ^{13}C NMR δ 23.20, 118.28, 124.63, 125.06, 125.51, 126.07, 126.52, 128.11, 128.57, 129.78, 133.71, 134.87, 138.03; IR (KBr) 3060, 3003, 2916, 1618, 1591, 1508, 1437, 852, 717, 617 cm^{-1}; Anal. Calcd for $C_{13}H_{10}Cl_2$: C, 65.85; H, 4.25. Found: C, 65.81; H, 4.44.

1,1-Dichloro-4-phenyl-2-phenethylbut-1-ene (4c) (Entry 3, Table 1). ^1H NMR δ 2.49-2.54 (m, 4H), 2.70-2.77 (m, 4H), 7.16-7.24 (m, 6H), 7.26-7.31 (m, 4H); ^{13}C NMR δ 33.30, 35.83, 116.65, 126.17, 128.29, 128.45, 137.94, 140.90; IR (neat) 3028, 2929, 1604, 1496, 1456, 897, 748, 698, 563, 494 cm^{-1}; Anal. Calcd for $C_{18}H_{18}Cl_2$: C, 70.83; H, 5.94. Found: C, 70.96; H, 6.03.

1,1-Dichloro-2-phenethylhex-1-ene (4d) (Entry 4, Table 1). ^1H NMR δ 0.92 (t, J= 7.3 Hz, 3H), 1.27-1.47 (m, 4H), 2.16-2.29 (m, 2H), 2.45-2.54 (m, 2H), 2.68-2.76 (m, 2H), 7.12-7.34 (m, 5H); ^{13}C NMR δ 13.87, 22.52, 29.31, 33.36, 33.47, 35.63, 115.59, 126.12, 128.29, 128.43, 138.82, 141.10; IR (neat) 3028, 2958, 2931, 2862, 1614, 1604, 1496, 1466, 1456, 895, 748, 698 cm^{-1}; Anal. Calcd for $C_{14}H_{18}Cl_2$: C, 65.38; H, 7.05. Found: C, 65.75; H, 7.15.

1,1-Dichloro-2,6,10-trimethylundec-1,5,9-triene (4e) (Entry 5, Table 1). ^1H NMR δ 1.59-1.63 (m, 4.7H), 1.67-1.71 (m, 4.3H), 1.86 and 1.87 (2s, 3H), 1.96- 2.19 (m, 6H), 2.23-2.31 (m, 2H), 5.05-5.16 (m, 2H); ^{13}C NMR δ 15.89, 17.62, 17.64, 19.97, 23.34, 25.35, 25.45, 25.66, 25.70, 26.57,

26.61, 31.86, 35.49, 35.83, 39.67, 114.42, 122.64, 123.56, 124.15, 124.22, 131.36, 131.61, 134.93, 136.36, 136.43; IR (neat) 2968, 2918, 2858, 1668, 1624, 1448, 1377, 897, 831 cm^{-1}; Anal. Calcd for $C_{14}H_{22}Cl_2$: C, 64.37; H, 8.49. Found: C, 64.27; H, 8.65.

1,1-Dichloro-2-pentylhept-1-ene (4f) (Entry 6, Table 1). ^1H NMR δ 0.90 (t, *J*= 7.0 Hz, 6H), 1.24-1.38 (m, 8H), 1.38-1.49 (m, 4H), 2.19-2.26 (m, 4H); ^{13}C NMR δ 13.98, 22.46, 26.87, 31.63, 33.45, 114.53, 139.76; IR (neat) 2956, 2927, 2873, 2860, 1614, 1466, 1379, 903, 885, 731 cm^{-1}; Anal. Calcd for $C_{12}H_{22}Cl_2$: C, 60.76; H, 9.35. Found: C, 61.11; H, 9.60.

1,1-Dichloro-2-methyltridec-1-ene (4g) (Entry 7, Table 1). ^1H NMR δ 0.88 (t, *J*= 6.9 Hz, 3H), 1.21-1.35 (m, 16H), 1.39-1.48 (m, 2H), 1.85 (s, 3H), 2.24 (t, *J*= 7.6 Hz, 2H); ^{13}C NMR δ 14.12, 19.79, 22.71, 26.98, 29.26, 29.37, 29.45, 29.57, 29.65, 29.66, 31.93, 35.41, 113.99, 135.34; IR (neat) 2960, 2937, 2858, 1624, 1468, 897 cm^{-1}; Anal. Calcd for $C_{14}H_{26}Cl_2$: C, 63.39; H, 9.88. Found: C, 63.78; H, 10.15.

1,1-Dichloro-2-ethyl-3-benzylbut-1-ene (4h) (Entry 8, Table 1). ^1H NMR δ 0.99 (d, *J*= 7.0 Hz, 3H), 1.08 (t, *J*= 7.6 Hz, 3H), 2.15-2.30 (m, 2H), 2.56 (dd, *J*= 13.4, 8.9 Hz, 1H), 2.75 (dd, *J*= 13.4, , 6.1 Hz, 1H), 3.18-3.26 (m, 1H), 7.13-7.30 (m, 5H); ^{13}C NMR δ 12.59, 17.19, 23.33, 39.94, 40.91, 115.60, 126.10, 128.23, 128.98, 139.77, 143.41; IR (neat) 3064, 3028, 2972, 2877, 1603, 1496, 1464, 1454, 918, 904, 741, 698 cm^{-1}; Anal. Calcd for $C_{13}H_{16}Cl_2$: C, 64.21; H, 6.63. Found: C, 64.46; H, 6.89.

1-Dichloromethylidene-3-phenylcyclohexane (4i) (Entry 9, Table 1). mp 45-46 °C; ^1H NMR δ 1.42-1.65 (m, 2H), 1.90-2.00 (m, 3H), 2.03-2.11 (m, 1H), 2.63 (br t, *J*= 12.2 Hz, 1H), 2.96 (d, *J*= 15.3 Hz, 1H), 3.08 (dd, *J*= 13.7, 1.8 Hz, 1H), 7.20-7.26 (m, 3H), 7.29-7.36 (m, 2H); ^{13}C NMR δ 26.21, 31.22, 33.51, 38.79, 44.25, 112.11, 126.42, 126.71, 128.50, 137.10, 145.54; IR (KBr) 3030, 2978, 2858, 1618, 1604, 1495, 1446, 916, 865, 755, 698 cm^{-1}; Anal. Calcd for $C_{13}H_{14}Cl_2$: C, 64.75; H, 5.85. Found: C, 64.75; H, 6.15.

1-Dichloromethylidene-4-*tert*-butylcyclohexane (4j) (Entry 10, Table 1). mp 55-56 °C (lit.[11] mp 53-54.5 °C); ^1H NMR δ 0.86 (s, 9H), 1.02-1.20 (m, 3H), 1.80-1.93 (m, 4H), 2.88-3.00 (m, 2H); ^{13}C NMR δ 27.43, 27.52, 31.68, 32.37, 47.50, 110.75, 137.94; IR (KBr) 2970, 2949, 2866, 1612, 1473, 1431, 1363, 870, 854 cm^{-1}; Anal. Calcd for $C_{11}H_{18}Cl_2$: C, 59.74; H, 8.20. Found: C, 59.36; H, 8.19.

Reaction of 1c with chloroform (2b) (Entry 2, Table 2). To an ice-cooled THF (3 mL) solution of **3** prepared from finely powdered molecular sieves 4A (200 mg), magnesium turnings (44 mg, 1.8 mmol), Cp_2TiCl_2 (448 mg, 1.8 mmol), and $P(OEt)_3$ (0.62 mL, 3.6 mmol) was added **2b** (0.07 ml, 0.9 mmol) dropwise, and the reaction mixture was stirred for 10 min. Then **1c** (72 mg, 0.3 mmol) in THF (2 mL) was added dropwise and the mixture was further stirred for 18 h. The usual workup gave 1-chloro-4-phenyl-2-phenethylbut-1-ene (**5b**) (57 mg, 70%) and **4c** (17 mg, 18%).

The Physical Properties of 1-chloro-1-alkenes 5. 1-Chloro-2,2-diphenylethene (5a) (Entry 1, Table 2). mp 39-40 °C (lit.[12] mp 41 °C); ^1H NMR δ 6.58 (s, 1H), 7.16-7.22 (m, 2H), 7.25-7.42 (m, 8H); ^{13}C NMR δ 115.83, 127.67, 127.93, 128.03, 128.16, 128.39, 129.83, 137.52, 140.07, 143.80; IR (KBr) 3076, 3059, 2927, 1593, 1576, 1495, 1442, 1032, 968, 943, 825, 808, 769, 754, 698, 627 cm^{-1}; Anal. Calcd for $C_{14}H_{11}Cl$: C, 78.32; H, 5.16. Found: C, 78.10; H, 5.35.

1-Chloro-4-phenyl-2-phenethylbut-1-ene (5b) (Entry 2, Table 2). ^1H NMR δ 2.31-2.38 (m, 2H), 2.52-2.58 (m, 2H), 2.69-2.79 (m, 4H), 5.83 (s, 1H), 7.10-7.16 (m, 2H), 7.16-7.25 (m, 4H), 7.25-7.33 (m, 4H); ^{13}C NMR δ 32.48, 33.31, 34.16, 36.95, 113.44, 126.01, 126.06, 128.26, 128.34, 128.36,

128.40, 141.18, 141.37, 141.50; IR (neat) 3029, 2927, 2860, 1633, 1603, 1496, 1454, 822, 795, 748, 698 cm^{-1}; Anal. Calcd for $C_{18}H_{19}Cl$: C, 79.84; H, 7.07. Found: C, 79.49; H, 7.14.

1-Chloro-2-phenethylhex-1-ene (5c) (Entry 3, Table 2). ^1H NMR δ 0.90 and 0.93 (2t, J = 7.1 Hz, 3H), 1.24-1.48 (m, 4H), 2.02-2.09 (m, 1H), 2.22-2.29 (m, 1H), 2.33-2.39 (m, 1H), 2.46-2.54 (m, 1H), 2.68-2.77 (m, 2H), 5.79 (s, 0.49H), 5.82 (s, 0.51H), 7.14-7.25 (m, 3H), 7.25-7.32 (m, 2H); ^{13}C NMR δ 13.85, 13.93, 22.28, 22.60, 29.23, 29.71, 29.96, 32.31, 33.32, 34.28, 34.75, 36.68, 112.49, 112.55, 125.93, 126.01, 128.27, 128.32, 128.39, 141.38, 141.69, 142.15, 142.19; IR (neat) 3028, 2958, 2931, 2862, 1633, 1604, 1496, 1456, 791, 744, 698 cm^{-1}; Anal. Calcd for $C_{14}H_{19}Cl$: C, 75.49; H, 8.60. Found: C, 75.24; H, 8.76.

1-Chloro-2-methyltridec-1-ene (5d) (Entry 4, Table 2; contaminated with 4g). ^1H NMR δ 0.88 (t, J= 6.9 Hz, 3H), 1.22-1.33 (m, 16H), 1.37-1.46 (m, 2H), 1.73 (d, J= 1.5 Hz, 0.66H), 1.76 (d, J= 1.5 Hz, 1.05H), 1.85 (s, 1.29H), 2.01-2.07 (m, 0.71H), 2.16-2.26 (m, 1.29H), 5.74-5.76 (m, 0.22H), 5.78 (q, J= 1.2 Hz, 0.35H); ^{13}C NMR δ 14.12, 16.34, 20.80, 22.70, 26.77, 27.49, 29.09, 29.34, 29.42, 29.49, 29.57, 29.59, 29.62, 29.65, 29.66, 31.79, 31.92, 37.09, 111.23, 111.59, 138.94, 138.96; IR (neat) 2956, 2925, 2854, 1466, 1379, 783, 721 cm^{-1}.

1-Chloro-2-ethyl-3-benzylbut-1-ene (5e) (Entry 5, Table 2). ^1H NMR δ 1.01(d, J= 6.4 Hz, 3H), 1.02-1.08 (m, 3H), 1.99-2.14 (m, 0.14H), 2.21 (dq, J= 13.3, 7.6 Hz, 0.93H), 2.26 (dq, J= 13.3, 7.6 Hz, 0.93H), 2.45-2.54 (m, 1.86H), 2.59 (dd, J= 13.4, 8.5 Hz, 0.07H), 2.73-2.84 (m, 1H), 3.26-3.35 (m, 0.07H), 5.73 (t, J= 1.5 Hz, 0.07H), 5.77 (s, 0.93H), 7.08-7.30 (m, 5H); ^{13}C NMR δ 12.33, 17.23, 18.86, 22.74, 23.66, 36.51, 40.65, 41.38, 42.10, 111.54, 112.72, 125.89, 125.99, 128.13, 128.19, 128.95, 129.04, 140.34, 146.88, 148.06; IR (neat) 3066, 3030, 2972, 2937, 2877, 1629, 1604, 1496, 1454, 810, 752, 698 cm^{-1}; Anal. Calcd for $C_{13}H_{17}Cl$: C, 74.81; H, 8.21. Found: C, 74.91; H, 8.50.

1-Chloromethylidene-3-phenylcyclohexane (5f) (Entry 6, Table 2). ^1H NMR δ 1.39-1.51 (m, 1H), 1.55-1.66 (m, 1H), 1.76-1.85 (m, 0.5H), 1.90-2.01 (m, 2.5H), 2.02-2.11 (m, 0.5H), 2.16-2.24 (m, 0.5H), 2.31-2.38 (m, 0.5H), 2.42-2.50 (m, 0.5H), 2.54-2.65 (m, 1H), 2.94-3.03 (m, 0.5H), 3.05-3.15 (m, 0.5H), 5.84 (t, J= 1.9 Hz, 0.49H). 5.86 (t, J= 1.8 Hz, 0.51H), 7.17-7.35 (m, 5H); ^{13}C NMR δ 26.15, 27.33, 27.88, 33.50, 33.91, 34.01, 35.64, 41.38, 44.16, 45.47, 109.37, 109.49, 126.26, 126.30, 126.68, 126.77, 128.44, 128.47, 141.11, 141.24, 145.95, 146.13; IR (neat) 3066, 3031, 2937, 2859, 1641, 1604, 1495, 1448, 972, 837, 793, 752, 700 cm^{-1}; Anal. Calcd for $C_{13}H_{15}Cl$: C, 75.54; H, 7.31. Found: C, 75.26; H, 7.17.

Reaction of 1c with chloroform-*d* (2c) (Entry 2, Table 3). To an ice-cooled THF (3 mL) solution of **3** prepared from finely powdered molecular sieves 4A (200 mg), magnesium turnings (44 mg, 1.8 mmol), Cp_2TiCl_2 (448 mg, 1.8 mmol), and $P(OEt)_3$ (0.62 mL, 3.6 mmol) was added **2c** (0.07 ml, 0.9 mmol) dropwise, and the reaction mixture was stirred for 10 min. Then **1c** (72 mg, 0.3 mmol) in THF (2 mL) was added dropwise and the mixture was further stirred for 18 h. The usual workup gave a mixture of 1-chloro-4-phenyl-2-phenethyl(1-^{2}H)but-1-ene (**6b**) and **5b** (57 mg). The yields of **6b** (63%) and **5b** (6%) were determined by NMR analysis.

The Physical Properties of 1-chloro-1-deuterio-1-alkenes 6. 1-Chloro-2,2-diphenyl[2-^{2}H]ethene (6a) (Entry 1, Table 3; contaminated with 5a). ^1H NMR δ 6.58 (s, 0.10H), 7.17-7.42 (m, 10H); ^{13}C NMR δ 115.56 (t, J= 30 Hz), 115.84, 127.68, 127.93, 128.03, 128.17, 128.39, 129.83, 137.52, 140.07, 143.70; IR (neat) 3081, 3032, 2293, 1645, 1591, 1495, 1442, 769, 758, 696, 628 cm^{-1}.

1-Chloro-4-phenyl-2-phenethyl[1-^{2}H]but-1-ene (6b) (Entry 2, Table 3; contaminated with 5b). ^1H NMR δ 2.30-2.36 (m, 2H), 2.49-2.57 (m, 2H), 2.67-2.78(m, 4H), 5.83 (s, 0.09H), 7.10-

7.15 (m, 2H), 7.15-7.24 (m, 4H), 7.24-7.32 (m, 4H); ^{13}C NMR δ 32.46, 33.31, 34.15, 35.83, 36.89, 36.94, 113.17 (t, *J*= 29 Hz), 113.46, 126.00, 126.06, 128.18, 128.27, 128.30, 128.34, 128.37, 128.41, 128.46, 140.91, 141.19, 141.22, 141.37, 141.51; IR (neat) 3062, 3026, 2925, 2860, 2293, 1616, 1603, 1496, 1454, 1030, 748, 698 cm^{-1}.

1-Chloro-2-phenethyl[1-^{2}H]hex-1-ene (6c) (Entry 3, Table 3; contaminated with 5c and 4d). ^{1}H NMR δ 0.87-0.95 (m, 3H), 1.19-1.48 (m, 4H), 2.05 (t, *J*= 7.6 Hz, 0.9H), 2.20-2.29 (m, 1.1H), 2.32-2.39 (m, 0.86H), 2.45-2.55 (m, 1.14H), 2.67-2.76 (m, 2H), 5.78 (s, 0.047H), 5.81 (s, 0.053H), 7.12-7.32 (m, 5H); ^{13}C NMR δ 13.84, 13.86, 13.93, 22.28, 22.52, 22.60, 29.24, 29.31, 29.71, 29.94, 29.97, 32.29, 32.32, 33.32, 33.36, 33.48, 34.28, 34.71, 34.76, 35.63, 36.63, 36.68, 112.22 (t, *J*= 30 Hz), 112.29 (t, *J*= 30 Hz), 112.51, 112.57, 115.59, 125.93, 126.02, 126.12, 128.27, 128.32, 128.39, 128.44, 138.83, 141.12, 141.39, 141.70, 142.02, 142.05, 142.16, 142.20; IR (neat) 3064, 3028, 2958, 2931, 2859, 2293, 1604, 1496, 1466, 1456, 744, 698 cm^{-1}.

1-Chloro-2-methyl[1-^{2}H]tridec-1-ene (6d) (Entry 4, Table 3; contaminated with 5d and 4g). ^{1}H NMR δ 0.88 (t, *J*= 7.0 Hz, 3H), 1.21-1.34 (m, 16H), 1.37-1.46 (m, 2H), 1.72 (s, 0.89H), 1.75 (s, 1.45H), 1.85 (s, 0.66H), 2.04 (t, *J*= 7.5 Hz, 0.97H), 2.17-2.26 (m, 1.03H), 5.74-5.76 (m, 0.038 H), 5.76-5.79 (m, 0.062H); ^{13}C NMR δ 14.10, 16.30, 16.34, 19.79, 20.73, 20.79, 22.70, 26.77, 26.97, 27.50, 29.11, 29.25, 29.35, 29.42, 29.50, 29.55, 29.57, 29.60, 29.65, 29.67, 29.71, 31.78, 31.81, 31.92, 33.33, 35.41, 35.87, 37.05, 37.10, 110.98 (t, *J*= 30 Hz), 111.25, 111.34 (t, *J*= 30 Hz), 111.62, 113.98, 116.70, 126.20, 128.30, 128.48, 135.38, 137.96, 138.78, 138.94, 140.93; IR (neat) 2927, 2852, 2293, 1626, 1466, 1377, 894, 756 cm^{-1}.

1-Chloro[^{2}H]methylidene-3-phenylcyclohexane (6e) (Entry 5, Table 3; contaminated with 5f (6e : 5f = 92.3 : 7.7). ^{1}H NMR δ 1.39-1.50 (m, 1.04 H), 1.55-1.66 (m, 0.96 H), 1.80 (dd, *J*= 13.7, 4.6 Hz, 0.48H), 1.89-2.01 (m, 2.56 H), 2.06 (dd, *J*= 13.3, 4.6 Hz, 0.48H), 2.19 (t, *J*= 13.4 Hz, 0.48H), 2.35 (br d, *J*= 13.6 Hz, 0.52 H), 2.45 (br d, *J*= 13.4 Hz, 0.48 H), 2.54-2.64 (m, 1 H), 2.98 (br d, *J*= 13.7 Hz, 0.48 H), 3.10 (br d, *J*= 13.4 Hz, 0.52 H), 5.84 (t, *J*= 1.8 Hz, 0.037 H), 5.86 (t, *J*= 1.8 Hz, 0.04H), 7.18-7.34 (m, 5 H); ^{13}C NMR δ 26.14, 27.32, 27.84, 27.87, 33.44, 33.49, 33.91, 34.01, 35.61, 41.33, 41.38, 44.16, 45.46, 109.09 (t, *J*= 30 Hz), 109.22 (t, *J*= 30 Hz), 109.37, 109.49, 126.26, 126.30, 126.67, 126.76, 128.43, 128.45, 140.95, 141.09, 141.23, 145.95, 146.12; IR (neat) 3062, 3027, 2933, 2891, 2291, 1628, 1603, 1495, 1448, 972, 955, 744, 698 cm^{-1}.

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