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Chlorination of Acyclic β-Diketones. Formation and Stability of β-Chloro-β,γ-unsaturated Ketones[1)]

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Chlorination of acyclic β-diketones with triphenylphosphine-carbon tetrachloride and the other chlorinating reagents predominantly afforded β-chloro-β,γ-unsaturated ketones except the cases of the terminal alkyl group of the diketones was methyl or *t*-butyl. In these reactions, the isomerization of the β-chloro-α,β-unsaturated ketones to the β,γ-unsaturated isomers was involved; the isomerization was achieved by triphenylphosphine-carbon tetrachloride as well as by some acid catalysts.

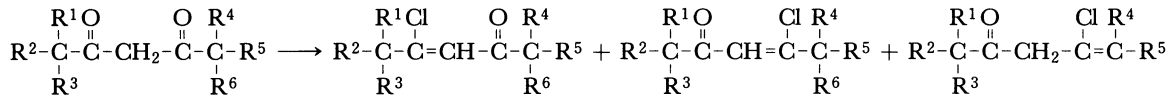
In our series of studies concerning reactions of β-diketones, the chlorination of β-diketones giving β-chloro-α,β-unsaturated ketones has attracted our attention. β-Chloro-α,β-unsaturated carbonyl compounds have become increasingly useful as intermediates in organic syntheses. For example, β-chloro-α,β-unsaturated ketones react with a zinc-silver couple in methanol,[2)] active methylene compounds,[3)] dimethylsulfoxonium methylide,[4)] and a nitrogen compound[5)] to produce a series of structurally diverse and potentially fruitful synthetic intermediates.

These β-chloro-α,β-unsaturated ketones were prepared by the chlorination of the corresponding β-diketones. However, the reactions hitherto reported were limited to those of cyclic β-diketones and 2,4-pentanedione.[2-13)] Thus, we were prompted to investigate the chlorination of some acyclic β-diketones. As the chlorinating reagents of β-diketones, a variety of reagents, phosphorus trichloride,[6-8)] phosgene,[9)] acetyl chloride,[10)] thionyl chloride,[7)] phosphoryl chloride,[6)] oxalyl dichloride,[2)] and dichlorotriphenylphosphorane,[12)] have been employed; however, triphenylphosphine in carbon tetrachloride was advantageously used to substitute the enol-hydroxyl group of β-diketones with a chlorine atom.[13)] This procedure is regarded as being superior to the others since the formation of hydrogen chloride is not involved; thus, essentially neutral conditions can be maintained throughout the reaction. We examined the chlorination of several acyclic β-diketones using this procedure with some modification.

Results and Disccusion

The β-diketones were treated with triphenylphosphine and carbon tetrachloride in chloroform or in an excess of carbon tetrachloride to give β-chloro-α,β-unsaturated and/or β-chloro-β,γ-unsaturated ketones (Table 1).

Table 1. Chlorination of β-Diketones



1 **2** **3** **4**

Run	Diketone	R^1	R^2	R^3	R^4	R^5	R^6	Reagent	Solvent	Chloro ketone[a)] Yield/%	**2** : **3** : **4**
1	**1a**	H	H	H	H	H	H	Ph_3P-CCl_4	CCl_4	96	100 : 0
2[b)]	**1a**							$(COCl)_2$	$CHCl_3$	50	100 : 0
3	**1a**							PCl_3	$CHCl_3$	25	100 : 0
4	**1b**	Me	H	H	Me	H	H	Ph_3P-CCl_4	$CHCl_3$	46(76)	20 : 80
5	**1b**							Ph_3P-CCl_4	CCl_4	27	17 : 83
6	**1b**							$(COCl)_2$	C_6H_6	36	27 : 73
7	**1b**							PCl_3	$CHCl_3$	0[c)]	
8	**1b**							$SOCl_2$	$CHCl_3$	0[d)]	
9	**1c**	Me	Me	H	Me	Me	H	Ph_3P-CCl_4	$CHCl_3$	45(70)	10 : 90
10	**1c**							$(COCl)_2$	$CHCl_3$	29	37 : 63
11	**1d**	Me	Me	Me	Me	Me	Me	Ph_3P-CCl_4	CCl_4	(7)[e,f)]	100 : 0
12	**1e**	H	H	H	Me	H	H	Ph_3P-CCl_4	CCl_4	(54)	35 : 12 : 53
13	**1f**	H	H	H	Me	Me	H	Ph_3P-CCl_4	CCl_4	(56)	67 : 4 : 29
14	**1g**	H	H	H	Me	Me	Me	Ph_3P-CCl_4	CCl_4	(29)[e,g)]	100 : 0 : 0

a) Yields are isolated yields, values indicated in parentheses are obtained by GLPC, and the isomer distributions are obtained from the crude products by GLPC. b) Lit.[2)] c) Unreacted diketone was recovered. d) Many unidentified products were obtained. e) Refluxed for 7 d. f) 26% of unreacted **1d** was recovered. g) 15% of **1g** was recovered.

Table 2. Isomerization between **2b** and **4b** in Chloroform

Catalyst	Starting material **2b** : **4b**	After 6 h at 60 °C **2b** : **4b**	After standing at room temp. overnight **2b** : **4b**
None	100 : 0	100 : 0	
Ph_3P–CCl_4	89 : 11	23 : 77	17 : 83
Ph_3P–CCl_4	2 : 98	12 : 88	14 : 86
Ph_3P	85 : 15	77 : 23	74 : 26
CF_3COOH	100 : 0	80 : 20	58 : 42
$AlCl_3$	100 : 0		57 : 43

4-Chloro-3-penten-2-one (**2a**) obtained from 2,4-pentanedione (**1a**) was a mixture of geometrical isomers ($E:Z$=85 : 15), which was confirmed by comparisons of their ^{1}H NMR spectra with the reported data.[14] Although β-chloro-α,β-unsaturated ketones were obtained from the corresponding β-diketones when the terminal alkyl group was methyl or *t*-butyl, 3,5-heptanedione (**1b**) and 2,6-dimethyl-3,5-heptanedione (**1c**) predominantly afforded unexpected β-chloro-β,γ-unsaturated ketones, 5-chloro-5-hepten-3-one (**4b**) and 5-chloro-2,6-dimethyl-5-hepten-3-one (**4c**) respectively. These ketones did not show the signal of a vinyl proton of the α,β-unsaturated ketone at around δ=6.5, but a singlet of methylene protons at δ=3.5 in their NMR spectra. These characteristic data, as well as their other NMR signals, indicate that the products are β-chloro-β,γ-unsaturated ketones. The **4b** obtained here was mainly a *Z* isomer, $Z:E$=89 : 11; its ^{13}C NMR spectrum indicated central methylene carbon signal at δ=52.60 and the γ-methyl signal at δ=14.27. These chemical shifts of the product were down-field compared with the respective values of its isomer (47.44 and 12.33), a small amount of which was detected in the product mixture in some cases but, unfortunately, could not be isolated. In a preliminary communication, we reported that the β-chloro-β,γ-unsaturated ketones were the exclusive product in these cases;[1] however, we later confirmed the formation of the α,β-unsaturated isomers (even in small amounts). There were some difficulties to separate the α,β-unsaturated isomers from the unreacted β-diketones. On the contrary, the β,γ-unsaturated ketones could be easily separated by column chromatography as well as GLPC. By increasing the steric bulkiness of the terminal alkyl groups of diketones, the reaction became very slow. The chlorination of **1d** resulted in only a product/unreacted diketone=7/12 after refluxing for 7 d.

In order to investigate the regioselectivity of the chlorination, unsymmetrical β-diketones were treated with triphenylphosphine and carbon tetrachloride in the same fashion. 2,4-Hexanedione (**1e**) gave a mixture of 5-chloro-4-hexen-3-one (**2e**), 4-chloro-3-hexen-2-one (**3e**) and 4-chloro-4-hexen-2-one (**4e**) in a ratio of 35 : 12 : 53. **4e** was mainly the *Z* isomer containing small amount of the *E* isomer similarly to **4b**. The chlorination of 5,5-dimethyl-2,4-hexanedione (**1g**) afforded a sole kind of α,β-unsaturated ketone. The ^{1}H NMR chemical shift of *t*-butyl group of the product (δ=1.14) was the same as that of the starting diketone (δ=1.14), and a long-range coupling (J=1.2 Hz) was observed between the methyl and the vinyl protons. Thus, the chlorination product was confirmed to be (*E*)-5-chloro-2,2-dimethyl-4-hexen-3-one (*E*-**2g**). The fact that the chlorination occurred at the acetyl moiety may be due to the steric bulkiness of the *t*-butyl group. The results obtained from these unsymmetrical diketones were comparable in the product distributions to that of symmetrical diketones. The chlorination of acetyl moiety gave only α,β-unsaturated ketones; however, the propionyl and isobutyryl groups were chlorinated, giving a mixtures of α,β- and β,γ-unsaturated isomers. Furthermore, the product ratios of α,β- and β,γ-unsaturated isomers, **3e** : **4e**=18 : 82 for propionyl group and **3f** : **4f**=12 : 88 for isobutyryl group, were quite equal to those obtained from symmetrical diketones, **2b** : **4b**=20 : 80 and **2c** : **4c**=10 : 90.

As control experiments, chlorination with oxalyl dichloride or phosphorus trichloride was pursued in the same way as reported.[2,3,7] The differences on isomeric ratio of the products in each preparation method was not so quite pronounced (Table 1), but triphenylphosphine-carbon tetrachloride system is superior to the other reagents regarding chemical yields.

As the enol form of β-diketones is considered to take an α,β-unsaturated ketone structure, the substitution of enol hydroxyl group of β-diketone by chlorine was expected to afford β-chloro-α,β-unsaturated ketone. In fact, **2b** was predominated over **4b** during an early stage of the chlorination reaction of **1b**; then, **4b** became superior as the reaction progresses. Thus, we undertook to examine the isomerization of the chlorinated products. The results are summarized in Table 2. When **2b** was heated at 60—65 °C in chloroform for 6 h, no isomerization could be observed at all. The isomerization from the α,β-unsaturated ketone **2b** to the β,γ-unsaturated isomer **4b**; however, it readily took place in the presence of triphenylphosphine and carbon tetrachloride, i.e. under the chlorination conditions, giving a mixture of 17% of **2b** and 83% of **4b**. A mixture of 14% of **2b** and 86% of **4b** was also obtained from **4b**. These values were almost identical with the isomeric ratio of the chlorination product. A slow isomerization was also achieved with acid catalysts,

CF_3COOH or $AlCl_3$, and triphenylphosphine alone. As a result of these experiments, it became clear that the β-chloro-β,γ-unsaturated ketone is thermodynamically more stable than its α,β-unsaturated isomer when a methyl group is substituted at the γ-position. The relative stabilities of the α,β- and β,γ-unsaturated carbonyl compounds have been discussed in terms of the conjugative and inductive contributions of substituents located on the three-carbon allylic chain;[15] however, very little is known about β-chloro-β,γ-unsaturated ketones and esters. Martin and Kirschleger indicated that the β-chloro-β,γ-unsaturated ketones preponderated over the α,β-unsaturated isomers in the Friedel-Crafts acylation products of alkylacetylenes with acetyl chloride.[16] Although the equilibrium between the α,β- and β,γ-unsaturated forms of the three-carbon allylic chain is not sensitive to the nature of the adjacent activating group as well as the alkyl substituents at the β-position, the alkyl substitution, particularly methyl substitution, at the γ-position increases the relative thermodynamic stability of the β,γ-unsaturated isomer.[15,17] More recently, Rhoads et al.[18] and Taskinen and Mukkala[19] reported that the introduction of a methoxyl group at the β-position strongly shifted the equilibrium towards the side of β,γ-unsaturated isomers.

In the present case, although the thermodynamic stability of β,γ-unsaturated ketones (**4**) may be primarily due to the γ-methyl substituent,[15] the similar effects to the β-methoxyl substituent would be expected for β-chloro substituent because the equilibration so strongly favored the β,γ-unsaturated isomer that would not have been expected on the basis of earlier analyses.[15] The initially formed β-chloro α,β-unsaturated ketones favored the *E* isomer. This fact may indicate a repulsive *cis* dipole-dipole interaction of the two polar functions, chloride and carbonyl, in the *Z* isomer is quite large. If the *Z* isomer exists in *s-trans* conformation, the repulsive dipole-dipole interaction would be diminished, but the steric repulsion between chlorine and the alkyl group attached to the carbonyl would contrary become prominent. In the *E* isomer of α,β-unsaturated ketones, a large steric repulsion between the ethyl or isopropyl group adjacent to the olefinic linkage and the acyl group destabilizes the *E* isomer. These steric and dipole-dipole interactions are relieved in the β,γ-unsaturated isomer. Thus, the chlorination products of **1b** and **1c** are favored β,γ-unsaturated ketone structures. On the other hand, as **2a** lacks γ-methyl substituent and also as the destabilizing *cis* steric interaction between methyl and acetyl groups would be overcome by the conjugative stabilization of α,β-unsaturated carbonyl system, **1a** gives only α,β-unsaturated **2a**.

Experimental

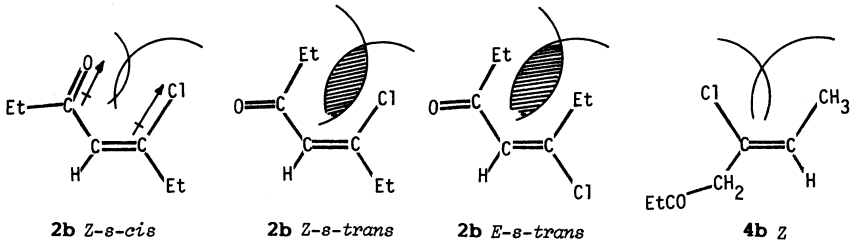
All bps were uncorrected. ^1H and ^{13}C NMR spectra were taken on JEOL PMX-60 and JNM-FX100 spectrometers respectively in $CDCl_3$ using TMS as an internal standard. IR spectra were measured with a Hitachi EPI-G2 spectrometer. MS spectra were taken on Hitachi M-80 mass spectrometer. GLPC analyses were performed on Hitachi 163 and 263 gas chromatographs using 3 mm×2 m columns packed with Silicone SE-30 30% on Shimalite or PEG-20M 20% on Chromosorb-W. Purifications of products were conducted by medium-pressure column chromatography on silica gel (Merck Kieselgel 60) or by atmospheric-pressure column chromatography on silica gel (Wakogel C-200).

Commercial GR grade 2,4-pentanedione was used after distillation, and the other β-diketones were prepared by reported methods.[20]

General Procedure for the Chlorination of β-Diketones. To a stirred mixture of 3,5-heptanedione (**1b**; 3.85 g, 30 mmol) and triphenylphosphine (15.7 g, 60 mmol), a solution of carbon tetrachloride (7.23 g, 47 mmol) in 55 ml of chloroform was added over a 5-min period. After the addition, the mixture was stirred at 60 °C for 6 h, then allowed to stand overnight at room temperature. The solvent was removed on a rotary evaporator under moderately reduced pressure. The residual viscous matter was extracted four times by grinding with 80 ml of pentane in a mortar finally leaving triphenylphosphine oxide and (dichloromethyl)triphenylphosphonium chloride as white crystalline powder. The extracts were combined and distilled to give a crude product, bp 95—104 °C/50 mmHg (1 mmHg=133.322 Pa), 3.5 g, which was a mixture of **1b** (4.1%), *E*-**2b** (16.3%), **4b** (77.2%), and *Z*-**2b** (2.4%) in order of GLPC retention times. The crude product was purified by moderate pressure column chromatography using hexane and hexane-ethyl acetate (98:2) as the eluent to obtain pure **2b** (0.27 g) and **4b** (1.74 g).

When the chlorination was pursued in excess carbon tetrachloride instead of chloroform solution, the GLPC-determined yields were almost comparable with the reaction in chloroform, however, we suffered some difficulties in the separation of products from the phosphonium salt and triphenylphosphine oxide.

(*Z*)-5-Chloro-5-hepten-3-one (*Z*-4b). Bp 86 °C/19 mmHg; ^1H NMR δ=1.07 (t, *J*=8 Hz, 3H), 1.78 (d, *J*=7 Hz, 1H), 2.57 (q, *J*=8 Hz, 2H), 3.39 (s, 2H), 5.72 (q, *J*=7 Hz, 1H); ^{13}C NMR δ=7.63 (q), 14.27 (q), 35.17 (t), 52.60 (t), 125.05 (s), 127.81 (d), 206.77 (s); IR (neat): 1660, 1720 cm^{-1}; MS: *m/z* 148 (M+2),



2b *Z-s-cis* **2b** *Z-s-trans* **2b** *E-s-trans* **4b** *Z*

146 (M^+), 117, 91, 89, 57; Found: C, 57.57; H, 7.65; Cl, 23.91%. Calcd for $C_7H_{11}OCl$: C, 57.34; H, 7.56; Cl, 24.18%.

(*E*)-5-Chloro-5-hepten-3-one (*E*-4b). Obtained as a mixture of *E*-**4b** and *Z*-**4b** (12 : 88). Bp 78 °C/20 mmHg; ^{13}C NMR δ=7.63 (q), 12.33 (q), 34.76 (t), 47.44 (t), 126.28 (s), 205.83 (s), a peak derived from C^5 could not be identified; Found: C, 57.54; H, 7.75; Cl, 24.35% (values obtained from the mixture).

(*E*)-5-Chloro-4-hepten-3-one (*E*-2b). ^1H NMR δ=1.06 (t, J=7 Hz, 3H), 1.16 (t, J=7 Hz, 3H), 2.49 (q, J=7 Hz, 2H), 2.96 (q, J=7 Hz, 2H), 6.35 (s, 1H); ^{13}C NMR δ=7.87 (q), 12.77 (q), 29.77 (t), 37.70 (t), 124.70 (d), 157.60 (s), 199.32 (s); IR (neat): 1600, 1690 cm^{-1}; Found: C, 57.16; H, 7.60; Cl, 23.99%.

(*Z*)-5-Chloro-4-hepten-3-one (*Z*-2b). ^1H NMR δ=1.20 (t, J=7 Hz, 3H), 1.30 (t, J=6 Hz, 3H), 2.47 (q, J=7 Hz, 2H), 2.60 (q, J=6 Hz, 2H), 6.21 (s, 1H); ^{13}C NMR δ=7.81 (q), 12.27 (q), 34.76 (t), 37.22 (t), 123.06 (d), 147.83 (s), 198.40 (s); IR (neat): 1610, 1705 cm^{-1}; Found: C, 57.40; H, 7.73; Cl, 24.29% (values obtained from a mixture of *Z*-**2b** and *Z*-**4b** (33 : 67)).

4-Chloro-3-penten-2-one (2a). Bp 63 °C/170 mmHg; ^1H NMR (*E*) δ=2.21 (s, 3H), 2.56 (d, J=1.1 Hz, 3H), 6.48 (q, J=1.1 Hz, 1H), (lit,[14] δ=2.20, 2.52, 6.47); (*Z*) δ=2.26 (s, 3H), 2.33 (s, 3H), 6.27 (s, 1H), (lit,[14] δ=2.26, 2.33, 6.27); IR (neat): 1610, 1700 cm^{-1} (lit,[14] 1610, 1705 cm^{-1}). The ratio *E* : *Z*= 85 : 15 was estimated from the peak area of GLPC.

5-Chloro-2,6-dimethyl-5-hepten-3-one (4c). Bp 113 °C/34 mmHg; ^1H NMR δ=1.13 (d, J=7 Hz, 6H), 1.71 (s, 3H), 1.84 (s, 3H), 2.64 (m, 1H), 3.57 (s, 2H); ^{13}C NMR δ=18.14 (q), 20.99 (q), 21.72 (q), 39.92 (d), 47.32 (t), 131.57 (s), 152.99 (s), 209.54 (s); Found: C, 61.92; H, 8.65; Cl, 19.82%. Calcd for $C_9H_{15}OCl$: C, 61.89; H, 8.66; Cl, 20.30%.

5-Chloro-2,6-dimethyl-4-hepten-3-one (2c). ^1H NMR δ= 1.25 (d, J=8 Hz, 6H), 1.30 (d, J=8 Hz, 6H), 2.60 (m, 2H), 2.75 (m, 2H), 6.38 (s, 1H); ^{13}C NMR δ=19.08 (q), 19.32 (q), 36.64 (d), 41.33 (d), 120.41 (d), 202.26 (s), a peak derived from C^5 could not be identified, (values obtained from a mixture with **4c**).

5-Chloro-2,2,6,6-tetramethyl-4-hepten-3-one (2d). ^1H NMR δ=1.17 (s, 9H), 1.26 (s, 9H), 6.57 (s, 1H); IR (neat): 1595, 1695 cm^{-1}; MS: *m/z* 204 (M+2), 202 (M^+), 147, 145, 117, 57.

5-Chloro-4-hexen-3-one (2e). ^1H NMR δ=1.07 (t, J=7 Hz, 3H), 2.48 (q, J=7 Hz, 2H), 2.54 (s, 3H), 6.39 (s, 1H); ^{13}C NMR δ=7.87 (q), 24.12 (q), 37.75 (t), 125.41 (d), 151.18 (s), 198.50 (s); IR (neat): 1605, 1695 cm^{-1}; Found: C, 54.21; H, 6.88; Cl, 26.87%. Calcd for C_6H_9OCl: C, 54.35; H, 6.84; Cl, 26.74%.

(*E*)-4-Chloro-3-hexen-2-one (*E*-3e). ^1H NMR δ=1.06 (t, J=7 Hz, 3H), 2.23 (s, 3H), 2.58 (q, J=7 Hz, 2H), 6.27 (s, 1H); ^{13}C NMR δ=7.81 (q), 28.30 (q), 37.10 (t), 124.64 (d), 142.08 (s), 198.85 (s); IR (neat): 1615, 1700 cm^{-1}. Acetyl proton signal, δ=2.23, was observed at almost the same chemical shift with *E*-**2a**, and very weak but clear signals expected to be derived from its *Z* isomer were observed in the ^{13}C NMR spectrum at δ=9.5, 29.2, and 138.4, thus the product was estimated to be *E* isomer.

(*Z*)-4-Chloro-4-hexen-2-one (*Z*-4e). ^1H NMR δ=1.78 (d, J=7 Hz, 3H), 2.14 (s, 3H), 3.37 (s, 2H), 5.69 (q, J=7 Hz, 1H); ^{13}C NMR δ=14.27 (q), 28.94 (q), 53.66 (t), 125.29 (d), 127.87 (s), 204.08 (s); IR (neat): 1660, 1725 cm^{-1}; Found: C, 54.45; H, 7.00; Cl, 26.51%. Calcd for C_6H_9OCl: C, 54.35; H, 6.84; Cl, 26.74% (values obtained from a mixture of **4e** and **3e** (92 : 8)). The product was almost a single isomer, estimated as a *Z* isomer by compairing its ^1H and ^{13}C NMR spectra with those of **4b**. Weak absorptions at δ=1.64 (d), 2.17 (s), 3.41 (s), 5.87 (s) (^1H NMR) and at δ=37.80, 47.61 (^{13}C NMR) indicated the contamination of small amount of the *E* isomer.

(*E*)-5-Chloro-2-methyl-4-hexen-3-one (*E*-2f). ^1H NMR δ= 1.13 (d, J=7 Hz, 6H), 2.28—2.83 (m, 1H), 2.58 (s, 3H), 6.54 (s, 1H); ^{13}C NMR δ=18.02 (q), 24.18 (q), 41.98 (d), 124.58 (d), 151.94 (s), 201.90 (s); IR (neat): 1605, 1695 cm^{-1}; Found: C, 57.55; H, 7.53; Cl, 23.89%. Calcd for $C_7H_{11}OCl$: C, 57.34; H, 7.56; Cl, 24.18%.

(*Z*)-5-Chloro-2-methyl-4-hexen-3-one (*Z*-2f). ^1H NMR δ= 1.13 (d, J=7 Hz, 6H), 2.77 (m, 1H), 2.28 (s, 3H), 6.39 (s, 1H); ^{13}C NMR δ=18.02 (q), 28.36 (q), 41.27 (d), 122.88 (d), 142.27 (s), 201.66 (s); IR (neat): 1610, 1695 cm^{-1}; Found: C, 57.29; H, 7.66; Cl, 23.90%.

4-Chloro-5-methyl-4-hexen-2-one (4f). ^1H NMR δ=1.78 (s, 3H), 1.89 (s, 3H), 2.17 (s, 3H), 3.46 (s, 2H); IR (neat): 1670, 1720 cm^{-1}; Found: C, 57.59; H, 7.72; Cl, 23.91%. Calcd for $C_7H_{11}OCl$: C, 57.34; H, 7.56; Cl, 24.18%.

(*E*)-5-Chloro-2,2-dimethyl-4-hexen-3-one (*E*-2g). ^1H NMR δ=1.15 (s, 9H), 2.52 (d, J=1.2 Hz, 3H), 6.62 (q, J=1.2 Hz, 1H); IR (neat): 1605, 1695 cm^{-1}; Found: C, 59.77; H, 8.22; Cl, 22.02%. Calcd for $C_8H_{13}OCl$: C, 59.81; H, 8.16; Cl, 22.07%.

Isomerization between 2b and 4b. A solution of **2b** (*E* : *Z*=55 : 1; 230 mg, 1.57 mmol), triphenylphosphine (828 mg, 3.14 mmol), carbon tetrachloride (490 mg, 3.14 mmol), tetralin (internal standard, 72 mg) in 5 ml of chloroform was kept at 57—60 °C for 6 h, then at room temperature overnight. The products distribution was analyzed by GLPC, giving the ratio of **2b** : **4b**=17 : 83. **4b** (contained 3% of **2b**, 168 mg, 1.15 mmol) was also treated as same as mentioned above yielding a mixture of **2b** : **4b**=14 : 86.

In the case of trifluoroacetic acid-catalyzed isomerization experiment, *E*-**2b** (147 mg, 1.0 mmol) and trifluoroacetic acid (104 mg, 0.91 mmol) was dissolved in 0.5 ml of $CDCl_3$, the solution in a NMR tube was kept at 53—57 °C for 5 h, and the ratio of **2b** and **4b** was obtained from the peak integrals of δ=6.35 (*E*-**2b**, 1H), 6.21 (*Z*-**2b**, 1H), and 3.39 (**4b**, 2H).

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