Hydrohalogenation Reaction of 1,2-Allenyl Ketones Revisited. Efficient and Highly Stereoselective Synthesis of *β,γ*-Unsaturated *β*-Haloketones

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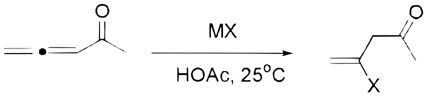
Introduction

β,γ-Unsaturated enones, which can be prepared via either a carbon−carbon or a carbon−oxygen double bond formation reaction,[1] are a class of compounds with high synthetic significance. However, their syntheses are compounded with difficulty due to the easy migration of the carbon−carbon double bond from the *β,γ*-position to the α,*β*-position.[1,2] Thus, efficient and stereoselective new synthetic routes to *β,γ*-unsaturated enones are of current interest.

Allenes have been found to have high and unique reactivities due to the existence of the two orthogonal *π*-bonds.[3,4] During the course of our study of allene chemistry, we rationalized from the retrosynthetic analysis that the hydrohalogenation reaction[5] of 1,2-allenyl ketones would be one of the most efficient methods for the synthesis of *β*-halogen substituted *β,γ*-unsaturated enones (Scheme 1).[6] However, the hydrochlorination reaction of 1,2-allenyl ketones by HCl was reported to lead to polymerization, and hydrochlorination using *N,N′*-dimethylhydrazine dihydrochloride or $SnCl_4$ afforded a mixture of *β,γ*-unsaturated and α,*β*-unsaturated *β*-chloroenones, favoring the α,*β*-enones.[2] Recently we disclosed in a brief note[7] that the hydrohalogenation reaction of 3,4-pentadien-2-one with metal halides in HOAc at room temperature selectively afforded 4-halo-4-penten-2-ones in high yields (eq 1). In this paper we wish to describe some of our recent results in this area.



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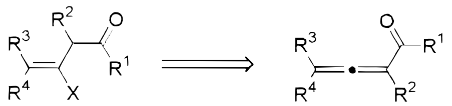
(1)

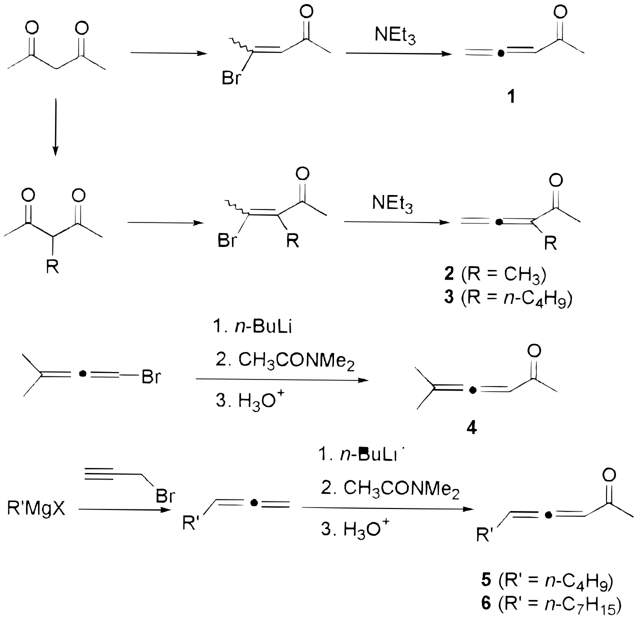
Results and Discussion

Synthesis of Starting Materials. 1,2-Allenyl ketones were prepared according to the corresponding known methods with modification (Scheme 2).[8−10] 3,4-Alkadien-2-ones **1**, **2**, and **3** were synthesized via the elimination of the corresponding 4-bromo-3-alken-2-ones.[8,9] Allenes **4**, **5**, and **6** were prepared via the reaction of the corresponding 1,2-allenyllithiums with CH_3CONMe_2.[10]

Scheme 1



Scheme 2



Hydrohalogenation Reaction of 3,4-Pentadien-2-one with LiI or NaI. The results of the reaction of 3,4-pentadien-2-one with LiI or NaI under different reaction conditions are summarized in Table 1. When the hydrohalogenation reaction with NaI was carried out in HOAc, with prelonged reaction time the amount of the isomerized α,*β*-unsaturated product **8** increased (compare entries 2 and 3, Table 1). The reaction can also occur in a 1:1 mixture of HOAc and THF. The ratio of *β,γ*-unsaturated enone **7** to α,*β*-unsaturated enone **8** is 87:13 (entry 4, Table 1), whereas in a 3 N solution of HOAc in THF at a lower reaction temperature the selectivity of the reaction is much higher (compare entries 5, 6, 9, and 10 with entries 1−4, 7, and 8, Table 1). The best results were obtained using MI (M = Na, Li) and HOAc (3 N) in THF at 0 °C (entries 9 and 10, Table 1).

Hydrohalogenation of 3-Alkyl-1,2-allenyl Ketones with MX. Surprisingly, the hydroiodination and hydrobromination reactions of 3-alkyl-1,2-allenyl ketones with MX in HOAc at 25 °C yielded the *Z*-isomer, i.e., ***Z*-9,** in

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[1] Tidwell, T. T. *Org. React.* **1990**, *39*, 297 and references therein.

[2] Gras, J.-L.; Galledou, B. S. *Bull. Soc. Chim. Fr.* **1983**, II-89.

[3] Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; John Wiley & Sons: New York, 1984.

[4] *The Chemistry of Ketenes, Allenes, and Related Compounds*, Part 1; Patai, S., Ed.; John Wiley & Sons: New York, 1980.

[5] For hydrohalogenation reaction of electron-deficient alkynes, see: Ma, S.; Lu, X. *J. Chem. Soc., Chem. Commun.* **1990**, 1643. Ma, S.; Lu, X. *Tetrahedron Lett.* **1990**, *31*, 7653. Ma, S.; Lu, X.; Li, Z. *J. Org. Chem.* **1992,** *57*, 709. Lu, X.; Zhu, G.; Ma, S. *Chin. J. Chem.* **1993**, *11*, 267. Ma, S.; Lu, X. *Org. Syn.* **1995**, *72*, 112. For a review, see: Lu, X.; Ma, S. *Chin. J. Chem.* **1998**, *16*, 388. For $ZrCl_4$-catalyzed three-component reaction of 1,2-allenyl ketones, aldehydes, and metallic halides, see: Zhang, C.; Lu, X. *Tetrahedron Lett.* **1997**, *38*, 4831.

[6] For the synthesis of (*Z*)-2-iodo-2-alkenyl ketones from 1-alkynyl ketones, see: Lou, F.-T.; Kumar, K. A.; Hsieh, L. C.; Mang, R. T. *Tetrahedron Lett.* **1994**, *35*, 2553.

[7] Ma, S.; Shi, Z.; Li, L. *J. Org. Chem.* **1998**, *63*, 4522. For some related studies of 2,3-allenyl carboxylic acid derivatives, see: Kurtz, von P.; Gold, H.; Disselnkoetter, H. *Justus Liebigs Ann.* **1959**, *624*, 1. Rosenquist, N. R.; Chapman, O. L. *J. Org. Chem.* **1976**, *41*, 3326. Font, J.; Gracia, A.; de March, P. *Tetrahedron* **1990**, *46*, 4407.

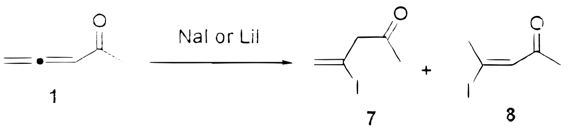
[8] Buono, G. *Synthesis* **1981**, 872.

[9] Buono, G. *Tetrahedron Lett.* **1972**, *32*, 3257.

[10] Clinet, J. C.; Linstrumelle, G. *Nouv. J. Chim.* **1977**, *1*, 373.

10.1021/jo9903205 CCC: $18.00

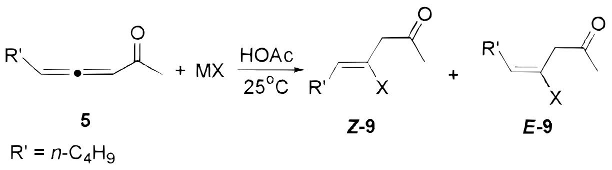
Table 1. Hydroiodination Reaction of 3,4-Pentadien-2-one



entry	MX	solvent	temp (°C)	time (h)	NMR yield (%)[a] 7	NMR yield (%)[a] 8	7/8
1	NaI	HOAc−MeCN	25	3	25	3	89/11
2	NaI	HOAc	25	3	44	3	94/6
3	NaI	HOAc	25	5	74	7	91/9
4	NaI	HOAc−THF(1:1)	25	5	58	9	87/13
5	NaI	HOAc (1 N)−THF	0	5	56	0.9	98/2
6	LiI	HOAc (1 N)−THF	0	5	63	2.2	97/3
7	NaI	HOAc (3 N)−THF	25	5	64	7	90/10
8	LiI	HOAc (3 N)−THF	25	5	59	7	89/11
9	LiI	HOAc (3 N)−THF	0	5	76	1.7	98/2
10	NaI	HOAc (3 N)−THF	0	10	79	1.9	98/2

[a] Determined by 300 MHz ^{1}H NMR spectra using CH_2Br_2 as the internal standard.

Scheme 3



MX	time (h)	product	NMR yield of *Z*-**9** (%)[a]	NMR yield of *E*-**9** (%)[a]
NaI	24	**9a**	90 (76)	3.6
LiBr[b]	38	**9b**	93 (82)	5
LiCl[b]	62	**9c**	25 (17)	55 (50)

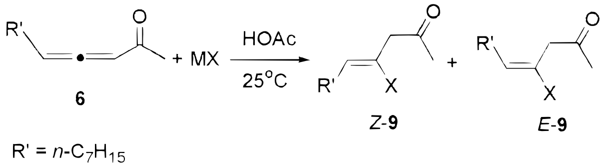
[a] The number in the parentheses are isolated yields.

[b] LiX monohydrate was used.

high yield with fairly good stereoselectivity, although the corresponding hydrochlorination reaction afforded the products **_E_-9** and **_Z_-9** with lower stereoselectivity (Schemes 3 and 4). The formation of α,β-unsaturated β-haloenones was not observed. The reaction of dodeca-3,4-dien-2-one with MX afforded similar results (Scheme 4). The configurations of the β,γ carbon−carbon double bonds were determined by the 2D NOESY spectra of **_E_-9c**/**_Z_-9c** and **_E_-9d**/**_Z_-9d** (Scheme 5). The reason for the different stereoselectivity with LiCl monohydrate is not clear.

Hydrohalogenation Reaction of 3,3-Dimethyl-Substituted 1,2-Allenyl Methyl Ketone with MX. Although 3,3-disubstituted 1,2-allenyl sulfones were found to be much less reactive toward MX in HOAc than 1,2-propadienyl sulfones,[11] the hydrohalogenation reaction of 5-methyl-3,4-hexadien-2-one (**4**) with MX (X = Cl, Br, I) also went smoothly to afford 4-halo-5-methyl-4-hexen-2-ones in high yields (Scheme 6). The β,γ carbon−carbon double bonds of **10** are stabilized by the four substituents;[1] thus, the formation of α,β-unsaturated enones was not observed.

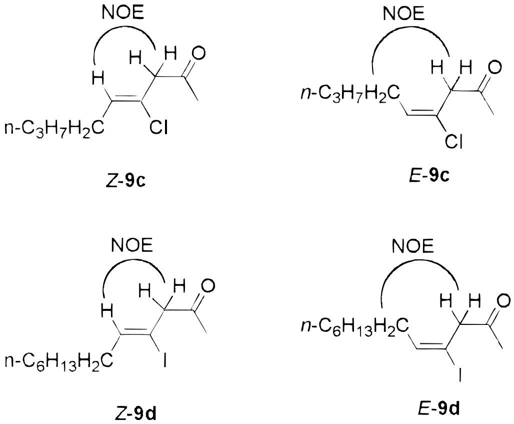
Scheme 4



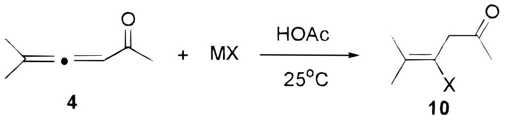
MX	time (h)	product	yield of *Z*-**9** (%)[a]	yield of *E*-**9** (%)[a]
NaI	36	**9d**	87	3.5
LiBr[b]	48	**9e**	75	3.1
LiCl[b]	72	**9f**	18	54

[a] Isolated yield. [b] LiX monohydrate was used.

Scheme 5



Scheme 6



MX	time (h)	product	yield (%) of **10**
NaI	25	**10a**	89
LiBr[a]	48	**10b**	90
LiCl[a]	48	**10c**	96

[a] LiX monohydrate was used.

Hydrohalogenation Reaction of 1-Substituted 1,2-Allenyl Ketones with MX. 1-Substituted 1,2-allenyl ketones reacted with MI (M = Na or Li) in HOAc afforded a mixture of β,γ-unsaturated β-iodoenone **11a** and α,β-unsaturated β-iodoenone **12a** with uninteresting ratio (entries 1 and 2, Table 2). The corresponding reaction in CF_3COOH afforded **11a** highly selectively, albeit in low yield (entry 3, Table 2). Using a 3 N solution of CF_3COOH in THF as the solvent greatly improved the yields, but the ratios of **11a**/**12a** still need optimizing (entries 4 and 5, Table 2). Finally we found that the reaction could afford the β,γ-unsaturated β-iodoenone **11a** highly selec-

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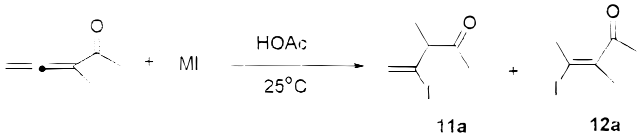
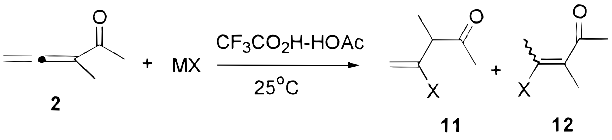
[11] For the results with 1,2-dienyl sulphones, see: Ma, S.; Wei, Q. *J. Org. Chem.* **1999**, *64*, 1026.

Table 2. Hydrohalogenation Reaction of 3-Methyl-3,4-pentadien-2-one



entry	MX	solvent	temp (°C)	time (h)	NMR yield (%) 11a	NMR yield (%) 12a	11a/12a
1	NaI	HOAc	50	22	25	55	31/69
2	NaI	HOAc	25	24	43	41	51/49
3	NaI	CF_3CO_2H	25	24	25	1.1	96/4
4	NaI	CF_3CO_2H (3 N)−THF	25	24	78	19	80/20
5	LiI	CF_3CO_2H (3 N)−THF	25	24	74	23	76/24
6	NaI	HOAc−CF_3CO_2H (1:1)	25	24	82	3	96/4
7	LiI	HOAc−CF_3CO_2H (1:1)	25	24	70	2	97/3

Scheme 7



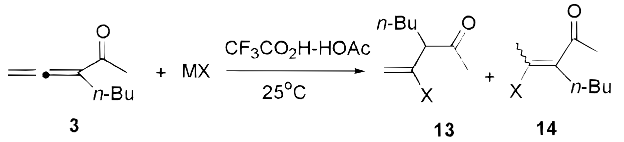
MX	NMR yield of **11** (%)[a]	NMR yield of **12** (%)[a, b]
LiBr[c]	75 (65) (**11b**)	5 (5) (**12b**)
LiCl[c]	70 (69) (**11c**)	5 (4) (**12c**)

[a] The number in the parentheses are isolated yields.

[b] Only one isomer was observed, and the configurations of the C = C bond of the minor products were not determined.

[c] LiX monohydrate was used.

Scheme 8



MX	Isolated yield of **13** (%)[a]	Isolated yield of **14** (%)[a,b]
NaI	89 (99) (**13a**)	(3.3)
LiBr[c]	85 (99) (**13b**)	(2.1)
LiCl[c]	74 (88) (**13c**)	(<2)

[a] The numbers in the parenthesis are NMR yields.

[b] Only one isomer was observed, and the configurations of the C = C bond of the minor products were not determined.

[c] LiX monohydrate was used.

tively when the reaction was carried out in a 1:1 mixture of CF_3COOH and HOAc (entries 6 and 7, Table 2).

Under these conditions, 3-methyl-3,4-pentadien-2-one also reacted smoothly with LiBr or LiCl and afforded the corresponding 4-halo-3-methyl-4-penten-2-ones **11** in high yields with high selectivity over the α,β-unsaturated enones **12** (Scheme 7).

The corresponding results of 3-butyl-3,4-pentadien-2-one were listed in Scheme 8.

The mechanism for the current regio- and/or stereoselective hydrohalogenation is a nucleophilic conjugate addition reaction of X^- with 1,2-allenyl ketones at the β-position to afford the expected β,γ-unsaturated β-haloketone product. As a result of the relatively mild acidic reaction conditions, the isomerization of the β,γ-unsaturated ketone to the α,β-unsaturated ketone is suppressed.

In conclusion, the methodology discussed in this paper provides an efficient general high-yielding route to β,γ-unsaturated β-haloketones with different substitution patterns. Because of the ease of converting the carbon−halogen bond, the carbonyl group, and the carbon−carbon double bond to other functional groups, this methodology will show its utility in the organic syntheses of compounds such as substituted β,γ-unsaturated enones, homoallylic alcohols, etc.

Experimental Section

General. Lithium iodide, lithium bromide monohydrate, lithium chloride monohydrate, NaI, THF, and CF_3COOH were commercially available and used without purification. ^1H NMR spectra were measured using $CDCl_3$ as the solvent and the internal standard. The NMR yields were measured using CH_2Br_2 as the internal standard.

Synthesis of 1,2-Allenyl Ketones. 3,4-Pentadien-2-one (**1**),[8] 3-methyl-3,4-pentadien-2-one (**2**),[8,9] 3-butyl-3,4-pentadien-2-one (**3**),[8,9] 5-methyl-3,4-hexadien-2-one (**4**),[10] 3,4-nonadien-2-one (**5**),[10,12] and 3,4-dodecadien-2-one (**6**)[10] were prepared according to the published procedures with modification.

3-Butyl-3,4-pentadien-2-one (3). Triethylamine (1.01 g, 10 mmol) was added to a stirred solution of 4-bromo-3-butyl-4-penten-2-one[8,13] (2.19 g, 10 mmol) in anhydrous CH_3CN (10 mL) at room temperature. Then, the mixture was refluxed for 20 h, diluted with ether, washed with 5% hydrochloric acid and cold water, and dried with magnesium sulfate. The solvent was evaporated and the residue was purified by chromatography on silica gel (eluent, pentane−ether = 200:1) to afford 0.745 g (54%) of **3**: liquid; ^1H NMR δ 0.87 (t, $J = 6.97$ Hz, 3 H), 1.20−1.42 (m, 4 H), 2.08−2.18 (m, 2 H), 2.27 (s, 3 H), 5.16 (t, $J = 2.91$ Hz, 2 H); MS (*m/e*) 138 (M^+, 3.02), 43 (100); IR (neat) 1927, 1676 cm^{-1}; HRMS calcd for $C_9H_{14}O$ 138.1045, found 138.1042.

3,4-Nonadien-2-one (5). 1,2-Heptadiene (1.92 g, 20 mmol) was treated with *n*-BuLi (20 mmol) in THF (20 mL) at −50 °C for 2 h, followed by the dropwise addition of *N,N*-dimethylacetamide (2.61 g, 30 mmol) at −78 °C, and reacted at this temperature for 2 h. The resulting solution was slowly transferred into an ice-cold aqueous HCl solution (0.1 N, 400 mL) and extracted with ether. Drying over $MgSO_4$, rotary evaporation, and chromatography on silica gel (eluent, pentane−ether = 40:1) afforded 1.46 g (53%) of the title compound:[12] liquid; ^1H NMR δ 0.90 (t, $J = 6.87$ Hz, 3 H), 1.33−1.48 (m, 4 H), 2.12−2.25 (m, 2 H), 2.21 (s, 3 H), 5.63 (q, $J = 6.68$ Hz, 1 H), 5,68−5.71 (m, 1 H); MS (*m/e*) 138 (M^+, 14.91), 43 (100); IR (neat) 1940, 1682 cm^{-1}.

3,4-Dodecadien-2-one (6). Liquid; ^1H NMR δ 0.87 (t, $J = 6.57$ Hz, 3 H), 1.26−1.49 (m, 10 H), 2.11−2.26 (m, 2 H), 2.21 (s, 3 H), 5.62 (q, $J = 6.58$ Hz, 1 H), 5.69−5.73 (m, 1 H), MS (*m/e*) 180 (M^+, 0.38); IR (neat) 1940, 1678 cm^{-1}. HRMS calcd for $C_{12}H_{20}O$ 180.1515, found 180.1514.

Hydroiodination Reaction of 3,4-Pentadien-2-one. NaI or LiI (2.2 mmol) was added to the solution of 3,4-pentadien-2-one (2.0 mmol) in the specified solvent (see Table 1), and the mixture was stirred for the time listed in Table 1. Then the mixture was diluted with ether and neutralized with aqueous K_2CO_3 at 0 °C. The ether layer was separated, the aqueous layer was extracted with ether, and the combined ether layers were dried over $MgSO_4$. Evaporation of the solvent afforded the crude

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(12) Ma, D.; Yu, Y.; Lu, X. *J. Org. Chem.* **1989**, *54*, 1105.

(13) Ono, N.; Yoshimura, T.; Saito, T.; Tamura, R.; Tanikaga, R.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1716.

product, which was analyzed by 300 MHz ^{1}H NMR spectroscopy using CH_2Br_2 as the internal standard. The spectral data of 4-iodo-4-penten-2-one are the same as reported in ref 7.

Synthesis of 4-Iodo-4-nonen-2-one (9a). Typical procedure. A solution of 3,4-nonadien-2-one (138 mg, 1.0 mmol) and NaI (180 mg, 1.2 mmol) in HOAc (1 mL) was stirred at 25 °C for 24 h. After complete conversion of the starting material as monitored by TLC, the mixture was diluted with ether and neutralized with aqueous K_2CO_3 at 0 °C. The ether layer was separated, the aqueous layer was extracted with ether, and the combined ether layers were dried over $MgSO_4$. Evaporation of the solvent and chromatography on silica gel (petroleum ether−ether = 100:1) afforded *Z*-**9a** in 76% yield (202 mg): liquid; ^{1}H NMR δ 0.91 (t, $J = 6.96$ Hz, 3 H), 1.34−1.54 (m, 4 H), 2.05−2.30 (m, 2 H), 2.18 (s, 3 H), 3.68 (s, 2 H), 5.65 (t, $J = 6.66$ Hz, 1 H); MS (*m*/*e*) 266 (M$^+$, 0.10), 43 (100); IR (neat) 1716, 1638 cm^{-1}; HRMS calcd for $C_9H_{15}IO$ 266.0169, found 266.0167. In the NMR spectra of the crude product, the following signals for the *E*-isomer were discernible: δ 3.67 (s, 2 H), 6.43 (t, $J = 7.34$ Hz, 1 H).

The following compounds were prepared similarly using the conditions listed in Schemes 3, 4, and 6.

(*Z*)-4-Bromo-4-nonen-2-one (9b). Liquid; ^{1}H NMR δ 0.90 (t, $J = 7.01$ Hz, 3 H), 1.27−1.50 (m, 4 H), 2.11−2.30 (m, 2 H), 2.19 (s, 3 H), 3.51 (s, 2 H), 5.82 (t, $J = 6.83$ Hz, 1 H), MS (*m*/*e*) 220 (M$^+$ (^{81}Br), 0.04), 218 (M$^+$ (^{79}Br), 0.05), 43 (100); IR (neat) 1715, 1649 cm^{-1}; HRMS calcd for $C_9H_{15}BrO$ 218.0307, found 218.0291. In the NMR spectra of the crude product, the following signals for the *E*-isomer were discernible: δ 3.61 (s, 2 H), 6.11 (t, $J = 7.61$ Hz, 1 H).

(*E*)-4-Chloro-4-nonen-2-one (9c).[14] Liquid; ^{1}H NMR δ 0.88 (t, $J = 7.01$ Hz, 3H), 1.23−1.50 (m, 4 H), 2.03 (q, $J = 7.24$ Hz, 2H), 2.21 (s, 3 H), 3.41 (s, 2 H), 5.84 (t, $J = 7.72$ Hz, 1 H); MS (*m*/*e*) 176 (M$^+$ (^{37}Cl), 12.34), 174 (M$^+$(^{35}Cl), 33.05), 43 (100); IR (neat) 1716, 1650 cm^{-1}.

(*Z*)-4-Chloro-4-nonen-2-one (9c).[14] Liquid; ^{1}H NMR δ 0.87 (t, $J = 6.99$ Hz, 3 H), 1.20−1.50 (m, 4 H), 2.10−2.30 (m, 2 H), 2.12 (s, 3 H), 3.42 (s, 2H), 5.62 (t, $J = 7.03$ Hz, 1 H); MS (*m*/*e*) 176 (M$^+$ (^{37}Cl), 2.39), 174 (M$^+$ (^{35}Cl), 6.80), 43 (100); IR (neat) 1717, 1652 cm^{-1}.

(*Z*)-4-Iodo-4-dodecen-2-one (9d). Liquid; ^{1}H NMR δ 0.87 (t, $J = 6.73$ Hz, 3 H), 1.15−1.53 (m, 10 H), 2.07−2.27 (m, 2 H), 2.11 (s, 3 H), 3.68 (s, 2 H), 5.65 (t, $J = 6.76$ Hz, 1 H); MS (*m*/*e*) 308 (M$^+$, 3.21), 43 (100); IR (neat) 1716, 1638 cm^{-1}; HRMS calcd for $C_{12}H_{21}IO$ 308.0638, found 308.0653. In the NMR spectra of the crude product, the following signals for the *E*-isomer were discernible: δ 3.72 (s, 2 H), 6.49 (t, $J = 7.52$ Hz, 1 H).

(*Z*)-4-Bromo-4-dodecen-2-one (9e). Liquid; ^{1}H NMR δ 0.87 (t, $J = 6.53$ Hz, 3 H), 1.18−1.52 (m, 10 H), 2.12−2.30 (m, 2 H), 2.20 (s, 3 H), 3.51 (s, 2 H), 5.82 (t, $J = 6.85$ Hz, 1 H); MS (*m*/*e*) 262 (M$^+$ (^{81}Br), 6.83), 260 (M$^+$ (^{79}Br), 6.83), 43 (100); IR (neat) 1716, 1652 cm^{-1}; HRMS calcd for $C_{12}H_{21}BrO$ 260.0776, found 260.0798. In the NMR spectra of the crude product, the following signals for the *E*-isomer were discernible: δ 3.55 (s, 2 H), 6.10 (t, $J = 7.64$ Hz, 1 H).

(*Z*)-4-Chloro-4-dodecen-2-one (9f). Liquid; ^{1}H NMR δ 0.87 (t, $J = 6.41$ Hz, 3H), 1.14−1.52 (m, 10 H), 2.10−2.30 (m, 2H), 2.20 (s, 3 H), 3.35 (s, 2 H), 5.63 (t, $J = 6.93$ Hz, 1 H); MS (*m*/*e*) 218 (M$^+$ (^{37}Cl), 0.02), 216 (M$^+$ (^{35}Cl), 0.04), 43 (100); IR (neat) 1716, 1654 cm^{-1}; HRMS calcd for $C_{12}H_{21}ClO$ 216.1282, found 216.1266.

(*E*)-4-Chloro-4-dodecen-2-one (9f). Liquid; ^{1}H NMR δ 0.86 (t, $J = 6.58$ Hz, 3 H), 1.15−1.60 (m, 10 H), 2.02 (q, $J = 7.35$ Hz, 2 H), 2.21(s, 3 H), 3.41 (s, 2 H), 5.84 (t, $J = 7.73$ Hz, 1 H); MS (*m*/*e*) 218 (M$^+$ (^{37}Cl), 1.94), 216 (M$^+$ (^{35}Cl), 5.85), 43 (100); IR (neat) 1716, 1650 cm^{-1}; HRMS calcd for $C_{12}H_{21}ClO$ 216.1282, found 216.1294.

4-Iodo-5-methyl-4-hexen-2-one (10a). Liquid; ^{1}H NMR δ 1.82 (s, 3 H), 2.00 (s, 3 H), 2.17 (s, 3 H), 3.80 (s, 2 H); MS (*m*/*e*) 238 (M$^+$, 24.12), 43 (100); IR (neat) 1716, 1632 cm^{-1}; HRMS calcd for $C_7H_{11}IO$ 237.9855, found 237.9865.

4-Bromo-5-methyl-4-hexen-2-one (10b). Liquid; ^{1}H NMR δ 1.77 (s, 3 H), 1.93 (s, 3H), 2.19 (s, 3 H), 3.63 (s, 2 H); MS (*m*/*e*) 192 (M$^+$(^{81}Br), 4.09), 190 (M$^+$(^{79}Br), 3.71), 43(100); IR (neat) 1710, 1650 cm^{-1}; HRMS calcd for $C_7H_{11}BrO$ 189.9992, found 189.9968.

4-Chloro-5-methyl-4-hexen-2-one (10c).[15,16] Liquid; ^{1}H NMR δ 1.75 (s, 3 H), 1.88 (s, 3 H), 2.18 (s, 3 H), 3.45 (s, 2 H); MS (*m*/*e*) 148 (M$^+$(^{37}Cl), 3.02), 146 (M$^+$(^{35}Cl), 5.71), 43 (100); IR (neat) 1715, 1655 cm^{-1}.

Synthesis of 4-Iodo-3-butyl-4-penten-2-one (13a). Typical procedure. NaI (180 mg, 1.2 mmol) was added to a solution of 3-butyl-3,4-pentadien-2-one (138 mg, 1 mmol) in HOAc (1 mL)−CF_3COOH (1 mL) at room temperature. The mixture was stirred at 25 °C for 24 h. After complete conversion of the starting material, the mixture was diluted with ether and neutralized with aqueous K_2CO_3 at 0 °C. The ether layer was separated, the aqueous layer was extracted with ether, and the combined ether layers were dried over $MgSO_4$. Evaporation of the solvent and chromatography on silica gel (petroleum ether−ether = 100:1) afforded **13a** in 89% yield (237 mg): liquid; ^{1}H NMR δ 0.89 (t, $J = 7.10$ Hz, 3 H), 1.05−1.44 (m, 4 H), 1.48−1.78 (m, 2 H), 2.19 (s, 3 H), 3.09 (dd, $J = 6.12$ and 8.20 Hz, 1 H), 6.02 (s, 1 H), 6.33 (s, 1 H); MS (*m*/*e*) 266 (M$^+$, 2.19); IR (neat) 1714, 1607 cm^{-1}; HRMS calcd for $C_9H_{15}IO$ 266.0169, found 266.0155. The following compounds were prepared similarly.

4-Bromo-3-butyl-4-penten-2-one (13b). Liquid; ^{1}H NMR δ 0.84 (t, $J = 7.05$ Hz, 3 H), 1.02−1.38 (m, 4 H), 1.54−1.88 (m, 2 H), 2.17 (s, 3 H), 3.26 (dd, $J = 6.17$ and 8.32 Hz, 1H), 5.65 (s, 1H), 5.79 (s, 1H); MS (*m*/*e*) 220 (M$^+$ (^{81}Br), 5.21), 218 (M$^+$ (^{79}Br), 5.36), 43 (100); IR (neat) 1715, 1621 cm^{-1}; HRMS calcd for $C_9H_{15}BrO$ 218.0307, found 218.0276.

3-Butyl-4-chloro-4-penten-2-one (13c). Liquid; ^{1}H NMR 0.87 (t, $J = 7.05$ Hz, 3 H), 1.06−1.39 (m, 4 H), 1.59−1.85 (m, 2 H), 2.20 (s, 3 H), 3.27 (dd, $J = 6.21$and 8.44 Hz, 1 H), 5.36 (s, 1 H), 5.41 (s, 1 H); MS (*m*/*e*) 176 (M$^+$(^{37}Cl), 3.15), 174 (M$^+$ (^{35}Cl), 9.14); IR (neat) 1715, 1626 cm^{-1}; HRMS calcd for $C_9H_{15}ClO$ 174.0813, found 174.0791.

4-Iodo-3-methyl-4-penten-2-one (11a). Liquid; ^{1}H NMR δ 1.19 (d, $J = 6.72$ Hz, 3 H), 2.19 (s, 3 H), 3.32 (q, $J = 6.72$ Hz, 1 H), 5.97 (s, 1 H), 6.30 (s, 1 H); MS (*m*/*e*) 224 (M$^+$, 10.90), 43 (100); IR (neat) 1710, 1605 cm^{-1}; HRMS calcd for C_6H_9IO 223.9698, found 223.9695.

4-Iodo-3-methyl-3-penten-2-one (12a). Liquid; ^{1}H NMR δ 2.07 (s, 3H), 2.27 (s, 3H), 2.67 (s, 3H); MS (*m*/*e*) 224 (M$^+$, 12.59), 43 (100); IR (neat) 1694, 1601 cm^{-1}; HRMS calcd for C_6H_9IO 223.9699, found 223.9707.

4-Bromo-3-methyl-4-penten-2-one (11b). Liquid; ^{1}H NMR δ 1.27 (d, $J = 6.86$ Hz, 3 H), 2.22 (s, 3 H), 3.41 (q, $J = 6.86$ Hz, 1 H), 5.66 (s, 1 H), 5.82 (s, 1 H); MS (*m*/*e*) 178 (M$^+$(^{81}Br), 1.50), 176 (M$^+$ (^{79}Br), 1.55); IR (neat) 1715, 1617 cm^{-1}; HRMS calcd for C_6H_9BrO 175.9837, found 175.9825.

4-Chloro-3-methyl-4-penten-2-one (11c).[17] Liquid; ^{1}H NMR δ 1.29 (d, $J = 6.96$ Hz, 3 H), 2.22 (s, 3 H), 3.44 (q, $J = 6.84$ Hz, 1 H), 5.37 (s, 1 H), 5.40 (s, 1 H); MS (*m*/*e*) 134 (M$^+$(^{37}Cl), 1.95), 132 (M$^+$ (^{35}Cl), 5.65), 43 (100); IR (neat) 1716, 1625 cm^{-1}.

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Supporting Information Available: The ^{1}H NMR spectra of the compounds ***Z*-9a−f**, ***E*-9c**, ***E*-9f**, **10a−b**, **11a−b**, **12a**, and **13a−c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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