Triethylborane Induced Radical Reaction of Ketene Silyl Acetals with Polyhalomethanes

Katsukiyo MIURA, Jiro SUGIMOTO, Koichiro OSHIMA,* and Kiitiro UTIMOTO*
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606
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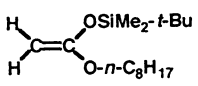
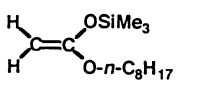
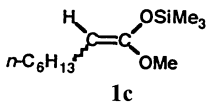
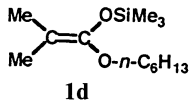
The treatment of ketene silyl acetal with tetrahalomethane or trihalomethane at room temperature in the presence of a catalytic amount of Et_3B provides 3,3-dihaloacrylate or (*E*)-3-haloacrylate, respectively. On the other hand, a reaction at −23 °C mainly gives 3,3,3-trihalopropanoate or 3,3-dihalopropanoate.

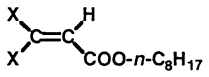
The addition of alkyl radicals to alkenes is one of the most important methodologies for synthesizing aliphatic C–C bonds via radical reactions. Recently, the development of a more efficient inter- or intramolecular radical addition has been the object of research in many laboratories.[1] Previously, we reported[2] that Et_3B[3] induced a radical addition of perfluoroalkyl iodides to ketone silyl enol ether, giving 2-perfluoroalkylated ketones. Ketene silyl acetals are more electron-rich olefins than ketone silyl enol ethers, and are good acceptors of electrophilic carbon radicals, such as perfluoroalkyl radicals.[2] Described herein is a further exploitation of this method regarding the reaction of polyhalomethanes[4] with ketene silyl acetals.[5]

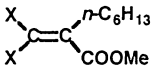
Results and Discussion

(1) Reaction of Ketene Silyl Acetals with Tetrahalomethanes. The reaction of ketene silyl acetal (**1a**, 2.0 mmol) with $CBrCl_3$ (1.0 mmol) at room temperature

Table 1. Reaction of Ketene Silyl Acetal with Tetrahalomethane[a]

Entry	Ketene silyl acetal	Tetrahalomethane	Reaction time/h	Product (Yield/%)[b] 2		3	
1	 **1a**	$CBrCl_3$	0.5	**2a**	(93)	**3a**	(0)
2		CCl_4	1.5	**2a**	(79)	**3a**	(0)
3		CBr_4	3	**2b**	(90)	**3b**	(0)
4		CF_2Br_2	0.5	**2c**	(84)	**3c**	(5)
5		CI_4	1	**2d**	(40)	**3d**	(0)[c]
6	 **1b**	$CBrCl_3$	0.5	**2a**	(78)	**3a**	(4)
7		CCl_4	1.5	**2a**	(71)	**3a**	(2)
8		CBr_4	3	**2b**	(87)	**3b**	(0)
9		CF_2Br_2	0.5	**2c**	(74)	**3c**	(10)
10	 **1c**	$CBrCl_3$	2	**2e**	(0)	**3e**	(90)
11		CCl_4	12	**2e**	(0)	**3e**	(56)
12		CBr_4	12	**2f**	(21)	**3f**	(44)[d]
13		CF_2Br_2	2	**2g**	(2)	**3g**	(86)
14	 **1d**	$CBrCl_3$	12	—	—	**3i**	(46)


2a: X=Cl, **2b**: X=Br, **2c**: X=F, **2d**: X=I

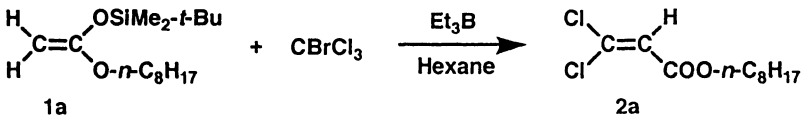

2e: X=Cl, **2f**: X=Br, **2g**: X=F

X_3CCH_2COO-*n*-C_8H_{17}
3a: X=Cl, **3b**: X=Br, **3d**: X=I
F_2BrCCH_2COO-*n*-C_8H_{17}
3c

X_3CCH(*n*-C_6H_{13})COOMe
3e: X=Cl, **3f**: X=Br
F_2BrCCH(*n*-C_6H_{13})COOMe
3g

$Cl_3CC(Me)_2COO$-*n*-C_6H_{13}
3i

a) Ketene silyl acetal (2.0 mmol), tetrahalomethane (1.0 mmol), and Et_3B (0.2 mmol), were employed. b) Yields based on tetrahalomethane. Entry 1—3, 8, 10, 11 and 14: Isolated yields. Entry 4—7, 9, 12 and 13: Yields are determined by the examination of ^1H NMR of the mixture of **2**, **3** and another product (Entry 5, 12) after purification. c) Octyl (*E*)-3-iodoacrylate (**4d**) was also obtained in 17% yield along with **2d**. d) Methyl 2-(dibromomethyl)octanoate (**5f**) was obtained in 4% yield in addition to **2f** and **3f**.



Scheme 1.

in the presence of Et_3B (0.2 mmol) gave octyl 3,3-dichloroacrylate (**2a**) in 93% yield (Scheme 1). Not only $CBrCl_3$, but also CX_4 (X=Cl, Br, I) or CF_2Br_2 easily reacted with **1a** to afford the corresponding octyl 3,3-dihaloacrylate **2a**, **2b**, **2d**, or **2c** (Table 1).[6] In the case of CF_2Br_2 (Entry 4 in Table 1), octyl 3-bromo-3,3-difluoropropanoate (**3c**) was obtained in 5% yield as a by-product, along with **2c**. The use of ketene trimethylsilyl acetal (**1b**) instead of **1a** slightly increased the ratio of product **3** to **2**.

The distribution of products **2** and **3** heavily depends on the reaction temperature (Table 2). Whereas the reaction of **1a** with $CBrCl_3$ at room temperature provided **2a** exclusively, the reaction at −23 °C gave **3a** as a major product (**2a**:**3a**=39:61). At −78 °C, the selectivity of products was improved and **3a** was obtained more than ten times as much as **2a** (**2a**:**3a**=9:91), even though the reaction proceeded slowly to afford the products in low yield (60%). A similar behavior has been observed in the reaction of **1b** with $CBrCl_3$. When the reaction was performed at room temperature, **2a** was mainly formed (**2a**:**3a**=95:5). On the other hand, the reaction of **1b** at −23 °C or −78 °C gave **3a** almost exclusively (**2a**:**3a**=5:95 or <2:>98). The decrease in the amount of **1b** (1.5 mmol per 1.0 mmol of $CBrCl_3$, Entry 9 in Table 2) did not influence the selectivity and yield of the products. However, the use of equimolar amounts of **1a** or **1b** (Entry 4 and 8) resulted in a decrease of the yields and selectivities.

The reaction of a ketene silyl acetal bearing alkyl group substituent (**1c**) with tetrahalomethanes afforded methyl 2-(trihalomethyl)octanoates (**3e—g**) as the major products, even at room temperature. Ketene silyl acetal **1d** reacted slowly with $CBrCl_3$ to give **3i** in poor yield because of its steric hindrance.

(2) Reaction of Ketene Silyl Acetals with Trihalomethanes. The treatment of ketene silyl acetal (**1a** or **1b**) with $CHBr_3$ provided a mixture of octyl (*E*)-3-bromoacrylate (**4b**) and octyl 3,3-dibromopropanoate (**5b**). Although trihalomethane, such as $CHXBr_2$ (X=Cl, F) or CHI_3, as well as $CHBr_3$, was applicable to this reaction,[7] $CHCl_3$ did not react with **1a** or **1b**. In any case, except for the reaction of $CHFBr_2$ with **1a**, 3-haloacrylate **4** was a major product at room temperature. Meanwhile, the reaction of any trihalomethane at −23 °C gave **5** preferentially and improved the combined yields of adducts **4** and **5**. The radical addition of trihalomethane to ketene silyl acetal having an alkyl substituent **1c** proceeded slowly and produced mainly **5**, even at room temperature.

3,3-Dihalopropanoates **5** were easily transformed into (*E*)-3-haloacrylates **4** by dehydrohalogenation with Et_3N. Thus, the addition of trihalomethane to **1a**, **1b**, or **1c** followed by treatment of the crude product with Et_3N afforded the corresponding **4**; the overall yields are shown in the last column of Table 3.

Table 2. Reaction of Ketene Silyl Acetal with $CBrCl_3$ under Various Conditions[a]

Entry	Ketene silyl acetal /mmol	Reaction temp/°C	Reaction time/h	Yield/%[b]	
				2a	**3a**
1	**1a** (2.0)	R.T.	0.5	93	0
2	**1a** (2.0)	−23	1	37	58
3	**1a** (2.0)	−78	8[c]	5	55
4	**1a** (1.0)	−23	1	32	19
5	**1b** (2.0)	R.T.	0.5	78	4
6	**1b** (2.0)	−23	1	5	91
7	**1b** (2.0)	−78	8[c]	<1	54
8	**1b** (1.0)	−23	1	5	64
9	**1b** (1.5)	−23	1	7	91

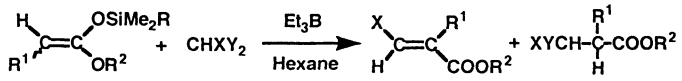
a) Ketene silyl acetal (1.0—2.0 mmol), $CBrCl_3$ (1.0 mmol), and Et_3B (0.2 mmol) were employed. b) Yields were determined by the examination of ^1H NMR of the mixture of **2a** and **3a** after purification. c) The reaction was stopped by the addition of galvinoxyl (0.0025 mmol) after stirring for 8 h.

As shown in Table 4, AIBN (azobisisobutyronitrile) also induced a radical addition of $CBrCl_3$ or $CHBr_3$ to ketene silyl acetal **1a** or **1b** to give **2a** or **4b** as a single product, respectively, without any contamination by **3a** or **5b**, though the yields were lower than those of a Et_3B induced reaction, especially in the case of the $CHBr_3$ reaction.

(3) Reaction of Ketene Silyl Acetals with 1,1,1-Tribromopropane or Ethyl Dibromoacetate. The use of 1,1,1-tribromopropane[8] or ethyl dibromoacetate in place of polyhalomethanes resulted in the formation of the corresponding 3-bromo-2-pentenoate (**6**) or fumarate (**8**) as a major product (Scheme 2). These polyhalo compounds were less reactive than polyhalomethanes and the yields of products were somewhat poor.

(4) Mechanism. In the presence of a radical scavenger, such as galvinoxyl,[9] Et_3B did not initiate the reaction of ketene silyl acetal **1a** with $CBrCl_3$. In addition, AIBN, as well as Et_3B, induced a reaction at 80 °C. These results support the idea that the Et_3B induced reaction includes a radical chain mechanism. Moreover, the formation of octyl acetate and *t*-$BuMe_2SiX$ (X=Br, Cl) was observed in addition to **2a** and **3a** in the reaction of **1a** and $CBrCl_3$. Thus, we were tempted to assume the following reaction mechanism for the formation of **2a** or **3a** (Scheme 3): (1) Ethyl

Table 3. Reaction of Ketene Silyl Acetal with Trihalomethane[a)]



1 4 5

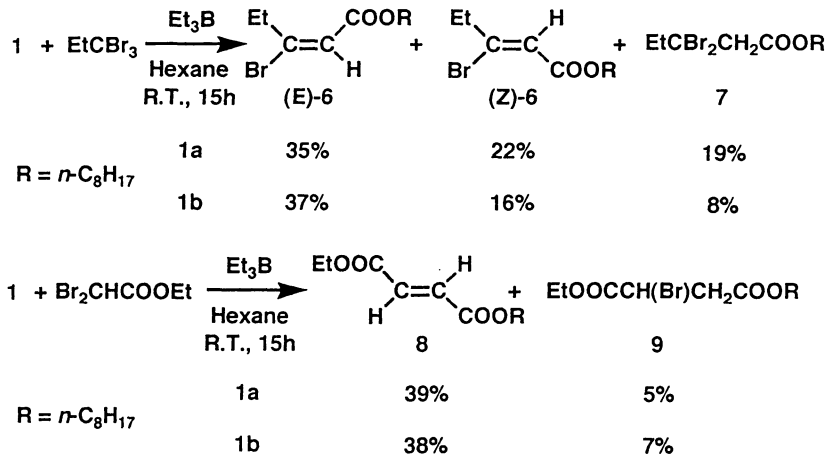
Entry	Ketene silyl acetal	$CHXY_2$ X	$CHXY_2$ Y	Reaction temp/°C	Reaction time/h	Product (Yield/%) $4^{b,c)}$	$5^{b)}$	$4^{c,d)}$
1	**1a**	Cl	Br	R.T.	3	**4a** (56)	**5a** (13)	
2	**1a**	Cl	Br	−23	3	**4a** (7)	**5a** (86)	**4a** (84)[e)]
3	**1a**	Br	Br	R.T.	3	**4b** (59)	**5b** (11)	
4	**1a**	Br	Br	−23	6	**4b** (10)	**5b** (79)	**4b** (79)
5	**1a**	F	Br	R.T.	1.5	**4c** (16)	**5c** (36)	
6	**1a**	F	Br	−23	6	**4c** (2)	**5c** (87)	**4c** (79)
7	**1a**	I	I	R.T[f)]	3	**4d** (37)	**5d** (4)	
8	**1b**	Cl	Br	R.T.	3	**4a** (60)	**5a** (4)	
9	**1b**	Cl	Br	−23	3	**4a** (10)	**5a** (84)	**4a** (88)[e)]
10	**1b**	Br	Br	R.T.	4	**4b** (60)	**5b** (9)	
11	**1b**	Br	Br	−23	6	**4b** (13)	**5b** (76)	**4b** (82)
12	**1b**	F	Br	R.T	1.5	**4c** (22)	**5c** (2)	
13	**1b**	F	Br	−23	6	**4c** (3)	**5c** (81)	**4c** (82)
14	**1b**	I	I	R.T.[f)]	3	**4d** (18)	**5d** (24)	
15	**1c**	Cl	Br	R.T.	12	**4e** (24)	**5e** (54)[g)]	**4e** (77)[e)]
16	**1c**	Br	Br	R.T.	12	**4f** (5)	**5f** (67)	**4f** (67)
17	**1c**	F	Br	R.T.	12	**4g** (2)	**5g** (20)[g)]	**4g** (21)

a) Ketene silyl acetal (2.0 mmol), trihalomethane $CHXY_2$ (1.0 mmol), and Et_3B (0.2 mmol) in hexane (5 ml) were employed. b) Yields based on trihalomethane were determined by the examination of ^1H NMR of the mixture of **4** and **5** after purification. c) (*Z*)-isomer of **4a**, **4b**, or **4d** was isolated in less than 2% yield. (*Z*)-isomer of **4c**, **4e**, **4f** or **4g** could not be detected. d) Treatment of crude product with Et_3N followed by purification afforded only **4**. e) **4a** or **4f** was obtained along with **4b** (5%) or **4e** (6%) respectively. f) At −23 °C, the reaction with CHI_3 is very slow. g) Diastereomeric mixture. **5e**; (50 : 50), **5g**, (55 : 45).

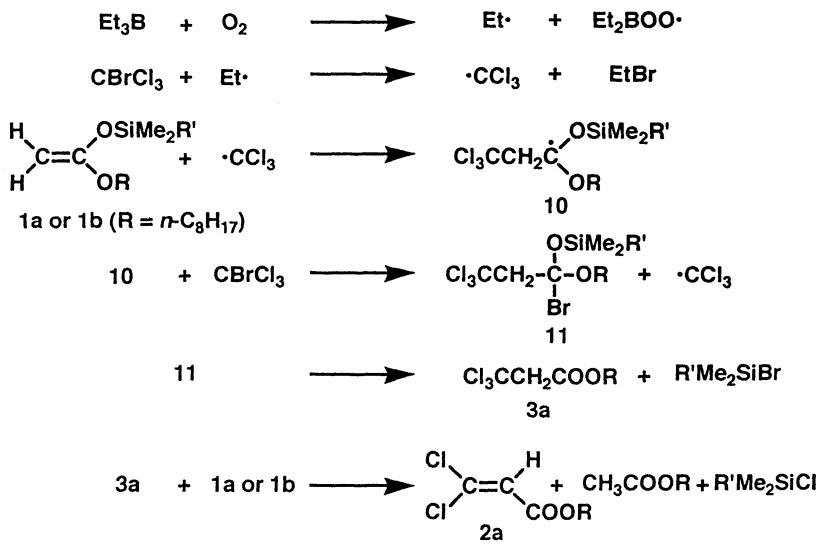
Table 4. AIBN Induced Reaction of Ketene Silyl Acetal with Polyhalomethane[a)]

Entry	Ketene silyl acetal	Polyhalomethane	Reaction time/h	Product (Yield/%)[b)]
1	**1a**	$CBrCl_3$	1	**2a** (85)
2	**1a**	$CHBr_3$	3	**4b** (28)
3	**1b**	$CBrCl_3$	1	**2a** (71)
4	**1b**	$CHBr_3$	3	**4b** (18)

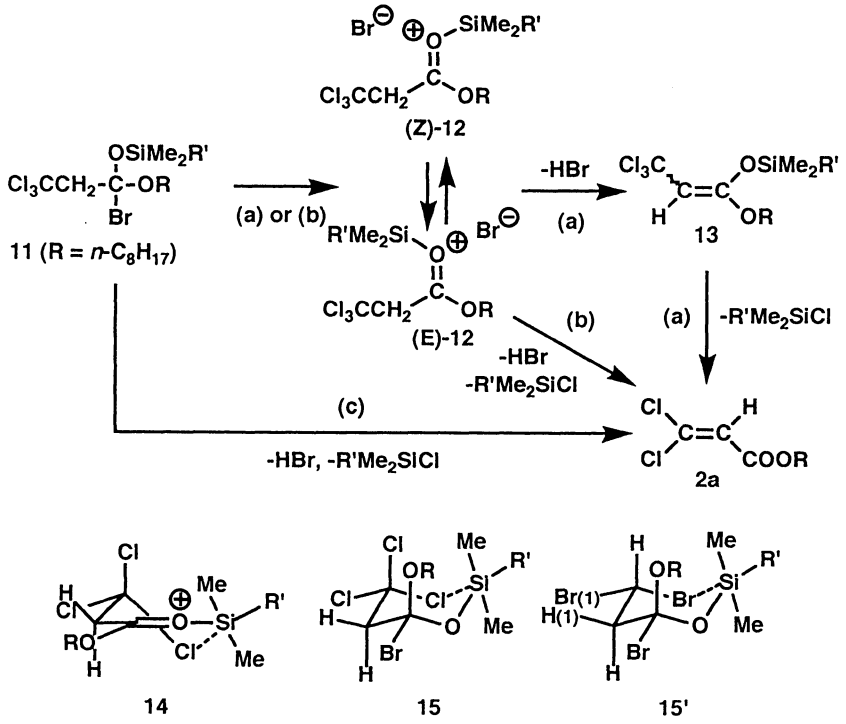
a) Ketene silyl acetal (2.0 mmol), polyhalomethane (1.0 mmol), and AIBN (0.1 mmol) were employed. All reactions were carried out at 80 °C in benzene. b) **3a** or **5b** could not be detected.



Scheme 2.



Scheme 3.



Scheme 4.

radical, generated by the action of molecular oxygen on Et_3B,[10] abstracts bromine from $CBrCl_3$ to give $\cdot CCl_3$; (2) the addition of $\cdot CCl_3$ to ketene silyl acetal (**1**) provides a new radical intermediate (**10**) which is a carbon radical bearing OR and $OSiMe_2R'$ groups;[2a] (3) intermediate **10** abstracts bromine from $CBrCl_3$ to afford an unstable bromide (**11**) and regenerates $\cdot CCl_3$; (4) elimination of silyl bromide leads **11** to 3,3,3-trichloropropanoates (**3a**); and (5) dehydrohalogenation of **3a** with excess **1** gives 3,3-dichloroacrylate (**2a**).

However, the last dehydrochlorination step (5) was denied in the following experiments. A mixture of $CBrCl_3$ and **1a** or **1b** was stirred for 1 h at −23 °C. Injection of a part of the reaction mixture to gas chromatography (glpc) revealed that **3a** was formed as a major product (**2a**:**3a**=4:6 or 5:95). The reaction mixture was then warmed to room temperature and stirred for another 1 h. A second injection of the reaction mixture to glpc showed that the ratio of **2a** to **3a** did not change, in spite of the presence of excess **1a** or **1b**. A similar result could be found in the reaction of $CHBr_3$ with **1b**. Moreover, treatment of **3a** with ketene

silyl acetal **1b** in hexane resulted in a complete recovery of **3a**. The addition of TMSBr to a reaction mixture of **3a** and **1b** also did not promote the formation of **2a**. These facts would suggest that **2a** is produced directly from the same intermediate **11** independently of the formation of **3a**.

The conceivable routes for the formation of **2a** from **11** are described in Scheme 4, though the mechanism is not clear at present. Path (**a**) or (**b**) involves an oxonium intermediate (**12**), which is derived from bromides **11** by the elimination of the Br^- anion. In path (**a**), deprotonation from **12** by ketene silyl acetal, followed by elimination of silyl chloride, affords **2a**. On the other hand, in path (**b**) the reaction proceeds through a 6-membered ring transition state (**14**) derived from the trans isomer of **12** to produce **2a**. The elimination of the silyl group and Cl is attributed to the high Lewis acidity of the silyl group. However, since it is difficult to assume the formation of such a polar intermediate as **12** in hexane, we propose an alternative path (**c**). The concerted anti elimination of HCl and $R'Me_2SiBr$ through a chair type 6-membered transition state possessing an axial alkoxyl group stabilized by an anomeric effect (**15**) gave **2a** directly.

The (*E*)-selective formation of the product in the reaction of ketene silyl acetal **1a** or **1b** with $CHBr_3$ could be explained in terms of the transition state model **15′**. In **15′**, bromine (1) occupies the equatorial position because of the steric repulsion of RO or the substituent silicon. The attack of ketene silyl acetal on equatorial hydrogen (1) causes a double anti elimination of HBr and $R'Me_2SiBr$ to afford octyl (*E*)-3-bromoacrylate (**4b**).

The temperature dependence of the distribution of products **2a** and **3a** could be explained as follows. The formation of **2a** includes the dehydrohalogenation of **11** or **12** by a second equivalent of ketene silyl acetal, which is favorable at room temperature. In contrast, this intermolecular reaction is slower than the elimination of $R'Me_2SiBr$ from **11** at low temperature, such as −78 °C, and **3a** becomes a major product.

Experimental

Distillation of the products was performed by use of Kugelrohr (Büchi), and boiling points are indicated by air-bath temperature without correction. ^{1}H NMR and ^{13}C NMR spectra were taken on a Varian XL-200 spectrometer, $CDCl_3$ was used as solvent, and chemical shifts being given in δ with tetramethylsilane as an internal standard. ^{19}F NMR spectra were recorded on JEOL JNM-FX 90Q spectrometer and the chemical shifts are given in δ with $CFCl_3$ as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer and the mass spectra on a Hitachi M-80 machine. When m/z is less than 100, mass spectra are described in only case where its relative intensity is more than 50. The analyses were carried out at the Elemental Analyses Center of Kyoto University.

Preparation of Ketene Silyl Acetal. Ketene silyl acetals **1a**—**d** were prepared by the reported procedure.[11] The physical data for **1a**—**d** are described in the literature.[2a]

Reaction of Ketene Silyl Acetal with Polyhalomethane. Typical procedure is as follows. Under argon atmosphere, Et_3B (0.96 M hexane solution, 0.21 ml, 0.20 mmol, M= mol dm^{-3}) was added to a solution of $CBrCl_3$ (0.20 g, 1.0 mmol) and ketene *t*-butyldimethylsilyl octyl acetal (0.57 g, 2.0 mmol) in hexane (5 ml) at room temperature (25±3 °C). After stirring for 30 min, sat. aq $NaHCO_3$ (5 ml) was added to the reaction mixture. The mixture was stirred vigorously for 1 h, then poured into water (20 ml), and extracted with hexane (20 ml×3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was purified by silica-gel column chromatography using hexane-ether (40 : 1) as an eluent to give octyl 3,3-dichloroacrylate (**2a**) in 93% yield: Bp 78—83 °C (1 Torr, 1 Torr=133.322 Pa, bath temp); IR (neat) 2954, 2924, 2854, 1735, 1605, 1466, 1297, 1171, 963, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.59—1.73 (m, 2H), 4.16 (t, *J*=6.7 Hz, 2H), 6.38 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=14.00, 22.58, 25.83, 28.44, 29.11 (two peaks), 31.71, 65.16, 120.05, 137.28, 162.31; MS (70 eV) m/z (rel intensity) 219 (M^++2−^{35}Cl, 6), 217 (M^+−^{35}Cl, 16), 143 (M^++2−C_8H_{15}, 39), 141 (M^+−C_8H_{15}, 62), 112(62), 111(27), 84(78), 83(71), 70(100), 69(55), 56(58). Found: C, 52.35; H, 7.36%. Calcd for $C_{11}H_{18}Cl_2O_2$: C, 52.19; H, 7.17%.

Octyl 3,3,3-Trichloropropanoate (3a): Bp 102—107 °C (1 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1749, 1467, 1346, 1284, 1180, 977, 715, 686 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.60—1.75 (m, 2H), 3.74 (s, 2H), 4.20 (t, *J*=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=14.06, 22.61, 25.81, 28.41, 29.10 (two peaks), 31.74, 57.85, 65.83, 92.72, 165.31; MS (70 eV) m/z (rel intensity) 179 (M^++2−C_8H_{15}, 9), 177 (M^+−C_8H_{15}, 9), 143(17), 141(29), 112(60), 111(16), 84(100), 83(71), 70(87), 69(42), 56(61). Found: C, 45.77; H, 6.65%. Calcd for $C_{11}H_{19}Cl_3O_2$: C, 45.62; H, 6.61%.

Octyl 3,3-Dibromoacrylate (2b): Bp 114—118 °C (2 Torr, bath temp); IR (neat) 2952, 2924, 2852, 1733, 1594, 1297, 1168 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.59—1.72 (m, 2H), 4.16 (t, *J*=6.7 Hz, 2H), 7.01 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=14.07, 22.62, 25.88, 28.46, 29.14 (two peaks), 31.74, 65.32, 106.35, 128.09, 163.14; MS (70 eV) m/z (rel intensity) 263 (M^++2−^{79}Br, 3), 261 (M^+−^{79}Br, 3), 233 (M^++4−C_8H_{15}, 24), 231 (M^++2−C_8H_{15}, 51), 229 (M^+−C_8H_{15}, 24), 215(38), 213(81), 211(42), 112(26), 84(58), 83(48), 70(84), 69(62), 56(82), 55(78), 43(90), 42(46), 41(100). Found: C, 38.86; H, 5.55%. Calcd for $C_{11}H_{18}Br_2O_2$: C, 38.62; H, 5.30%.

Octyl 3,3-Difluoroacrylate (2c): Bp 69—73 °C (9 Torr, bath temp); IR (neat) 2954, 2926, 2856, 1749, 1734, 1711, 1357, 1279, 1137 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.58—1.72 (m, 2H), 4.15 (t, *J*=6.7 Hz, 2H), 4.98 (dd, *J*=21.8, 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.97, 22.58, 25.80, 28.47, 29.12 (two peaks), 31.72, 64.98, 77.10 (dd, *J*=28.6, 9.1 Hz), 161.87 (dd, *J*=311.7, 298.5 Hz), 162.97 (dd, *J*=17.1, 7.5 Hz); ^{19}F NMR ($CDCl_3$) δ=−64.74 (dd, *J*=21.7, 15.8 Hz, 1F), −70.85 (dd, *J*=15.8, 2.0 Hz, 1F); MS (70 eV) m/z (rel intensity) 112(7), 109(M^+−C_8H_{15}, 26), 91(M^+−C_8H_{15}−H_2O, 100), 43(52), 41(51). Found: C, 60.12; H, 8.47%. Calcd for $C_{11}H_{18}F_2O_2$: C, 59.98; H, 8.24%.

Octyl 3-Bromo-3,3-difluoropropanoate (3c): Bp 67—71 °C (1 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1750, 1356, 1285, 1218, 1176, 1092, 1024 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89

(t, J=6.4 Hz, 3H), 1.28 (bs, 10H), 1.58—1.72 (m, 2H), 3.45 (t, J=13.2 Hz, 2H), 4.18 (t, J=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=14.06, 22.61, 25.74, 28.36, 29.09 (two peaks), 31.73, 49.11 (t, J=23.5 Hz), 66.00, 116.36 (t, J=305.9 Hz), 164.48 (t, J=4.5 Hz); ^{19}F NMR ($CDCl_3$) δ=−44.15 (t, J=13.3 Hz); MS (70 eV) m/z (rel intensity) 191 (M^++2−C_8H_{15}, 3), 189(M^+−C_8H_{15}, 3), 173 (M^++2−C_8H_{15}−H_2O, 11), 171 (M^+−C_8H_{15}−H_2O, 14), 145(12), 143(13), 112(11), 84(63), 71(50), 70(82), 69(60), 57(76), 56(91), 55(80), 43(91), 42(60), 41 (100). Found: C, 44.02; H, 6.42%. Calcd for $C_{11}H_{19}BrF_2O_2$: C, 43.87; H, 6.36%.

Octyl 3,3-Diiodoacrylate (2d): Bp 139—143 °C (0.31 Torr, bath temp), IR (neat) 2950, 2922, 2852, 1727, 1570, 1291, 1252, 1168, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.28 (bs, 10H), 1.60—1.72 (m, 2H), 4.14 (t, J=6.7 Hz, 2H), 7.80 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=14.07, 22.58, 25.85, 28.43, 29.10 (two peaks), 31.70, 65.14, 140.43, 164.51 (Another olefinic ^{13}C could not be detected.); MS (70 eV) m/z (rel intensity) 436 (M^+, 4), 325 (M^+−C_8H_{15}, 44), 324(100), 307(61), 279(14), 197(12), 152(28), 127(12), 43(80), 41(63). Found: C, 30.57; H, 4.20%. Calcd for $C_{11}H_{18}I_2O_2$: C, 30.30; H, 4.16%.

Methyl 2-(Trichloromethyl)octanoate (3e): Bp 92—97 °C (3 Torr, bath temp), IR (neat) 2954, 2924, 2856, 1752, 1458, 1436, 1349, 1257, 1202, 1165, 779, 722, 668 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.20—1.45 (m, 8H), 1.91—2.19 (m, 2H), 3.48 (dd, J=10.2, 4.0 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=13.92, 22.43, 26.88, 28.72, 30.23, 31.39, 52.23, 65.58, 98.17, 169.33; MS (70 eV) m/z (rel intensity) 241 (M^++2−^{35}Cl, 5), 239 (M^+−^{35}Cl, 8), 159 (M^++4−^{35}Cl−C_6H_{12}, 10), 157 (M^++2−^{35}Cl−C_6H_{12}, 68), 155 (M^+−^{35}Cl−C_6H_{12}, 100), 116(18), 109(10), 107(10). Found: C, 43.72; H, 6.32%. Calcd for $C_{10}H_{17}Cl_3O_2$: C, 43.58; H, 6.22%.

Methyl 3,3-Dibromo-2-hexylacrylate (2f): Bp 74—78 °C (1 Torr, bath temp); IR (neat) 2952, 2926, 2856, 1733, 1457, 1434, 1278, 1247, 1194, 1136, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.4 Hz, 3H), 1.25—1.60 (m, 8H), 2.40—2.48 (m, 2H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=14.01, 22.47, 26.97, 28.64, 31.39, 35.75, 52.53, 93.54, 140.99, 167.20; MS (70 eV) m/z (rel intensity) 260 (M^++4−C_5H_{10}, 8), 258 (M^++2−C_5H_{10}, 17), 256 (M^+−C_5H_{10}, 9), 249 (M^++2−^{79}Br, 34), 247 (M^+−^{79}Br, 39), 245(25), 179(25), 177(26), 135(21), 107(75), 43(100), 41(54). Found: C, 36.88; H, 5.07%. Calcd for $C_{10}H_{16}Br_2O_2$: C, 36.61; H, 4.92%.

Methyl 2-(Tribromomethyl)octanoate (3f): Bp 88—93 °C (2 Torr, bath temp); IR (neat) 2952, 2926, 2856, 1746, 1457, 1434, 1343, 1255, 1200, 1164, 701, 627 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (t, J=6.5 Hz, 3H), 1.20—1.50 (m, 8H), 1.93—2.25 (m, 2H), 3.56 (dd, J=10.1, 3.8 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=14.00, 22.48, 26.78, 28.78, 31.44, 32.94, 39.11, 52.22, 67.79, 170.09; MS (70 eV) m/z (rel intensity) 331 (M^++4−^{79}Br, 2), 329 (M^++2−^{79}Br, 4), 327 (M^+−^{79}Br, 3), 247 (M^++4−^{79}Br−C_6H_{12}, 6), 245 (M^++2−^{79}Br−C_6H_{12}, 12), 243 (M^+−^{79}Br−C_6H_{12}, 6), 169(22), 109(31), 107(39), 59(62), 43(100), 41(94), 39(57). Found: C, 29.61; H, 4.17%. Calcd for $C_{10}H_{17}Br_3O_2$: C, 29.37; H, 4.19%.

Methyl 3,3-Difluoro-2-hexylacrylate (2g): Bp 90—95 °C (35 Torr, bath temp); IR (neat) 2956, 2928, 2858, 1749, 1716, 1440, 1347, 1195, 1157, 1129, 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.4 Hz, 3H), 1.25—1.53 (m, 8H), 2.18—2.27 (m, 2H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=13.95, 22.52, 24.46, 28.50, 28.65, 31.45, 51.95, 88.74 (dd, J=24.4, 3.7 Hz), 159.78 (dd, J=309.8, 294.5 Hz), 165.53 (dd, J=12.2, 5.4 Hz); ^{19}F NMR ($CDCl_3$) δ=−70.23 (s, 1F), −75.05 (s, 1F); MS (70 eV) m/z (rel intensity) 186 (M^+−HF, 4), 175 (M^+−OMe, 17), 144(34), 143(61), 127(20), 107(24), 105(34), 101(43), 43(100), 41(55). Found: C, 58.19; H, 8.07%. Calcd for $C_{10}H_{16}F_2O_2$: C, 58.24; H, 7.82%.

Methyl 2-(Bromodifluoromethyl)octanoate (3g): Bp 76—80 °C (7 Torr, bath temp); IR (neat) 2954, 2926, 2858, 1752, 1459, 1437, 1347, 1259, 1198, 1170, 1096, 951, 933 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.3 Hz, 3H), 1.30 (bs, 8H), 1.73—2.06 (m, 2H), 3.27 (td, J=10.8, 4.3 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3$) δ=13.91, 22.44, 26.69, 27.76, 28.72, 31.35, 52.50, 58.54 (t, J=20.9 Hz), 120.44 (t, J=309.2 Hz), 168.35 (t, J=3.9 Hz); ^{19}F NMR ($CDCl_3$) δ=−47.63 (dd, J=158.0, 10.8 Hz, 1F), −48.33 (dd, J=158.0, 10.8 Hz, 1F); MS (70 eV) m/z (rel intensity) 257 (M^++2−OMe, 1), 255 (M^+−OMe, 1), 207 (M^+−^{79}Br, 21), 127(10), 123(100), 107(11), 43(56), 41(51). Found: C, 41.94; H, 6.04%. Calcd for $C_{10}H_{17}BrF_2O_2$: C, 41.83; H, 5.97%.

Hexyl 3,3,3-Trichloro-2,2-dimethylpropanoate (3i): Bp 88—93 °C (1 Torr, bath temp); IR (neat) 2954, 2930, 2858, 1737, 1469, 1257, 1155, 901, 795, 743, 638 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.25—1.46 (m, 6H), 1.60—1.76 (m, 8H, including 1.64 (s, 6H)), 4.17 (t, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.89, 22.43, 23.24, 25.52, 28.28, 31.24, 59.92, 65.95, 104.83, 170.62; MS (12 eV) m/z (rel intensity) 211 (M^++6−C_6H_{11}, 0.4), 209 (M^++4−C_6H_{11}, 5), 207 (M^++2−C_6H_{11}, 15), 205 (M^+−C_6H_{11}, 14), 171(15), 169(22), 133(11), 126(38), 124(56), 85(60), 84(100), 43(73). Found: C, 45.69; H, 6.70%. Calcd for $C_{11}H_{19}Cl_3O_2$: C, 45.62; H, 6.61%.

Stereochemistry of 3-Haloacrylate Derivatives. Stereochemistry of octyl (*E*)-3-haloacrylates **4a—d** was determined by the examination of the ^{1}H NMR chemical shifts and coupling constants of olefinic protons. The assignment of methyl (*E*)-3-halo-2-hexylacrylates **4e—g** was also based on inspection of chemical shift of olefinic proton. The δ values of olefinic proton of **4e—g** are similar to that of proton on 3-position of the respective octyl (*E*)-3-haloacrylate **4a—c**. In addition, the comparison of the ^{1}H NMR spectra of **4f** with methyl (*E*) or (*Z*)-3-bromo-2-methylacrylate[12] supported that **4f** had (*E*)-stereochemistry. Methyl (*E*)-3-bromo-2-methylacrylate ($CDCl_3$) δ=2.01 (d, J=1.7 Hz, 3H), 3.77 (s, 3H), 7.54 (q, J=1.7 Hz, 1H). (*Z*)-isomer (minor product) ($CDCl_3$) δ=2.00 (d, J=1.6 Hz, 3H), 3.82 (s, 3H), 6.57 (q, J=1.6 Hz, 1H). Methyl (*E*)-3-bromo-2-hexylacrylate (**4f**) ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.25—1.55 (m, 8H), 2.43—2.51 (m, 2H), 3.76 (s, 3H), 7.51 (s, 1H).

Octyl (*E*)-3-Chloroacrylate (4a): Bp 69—74 °C (1 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1726, 1612, 1296, 1254, 1161 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=6.3 Hz, 3H), 1.28 (bs, 10H), 1.59—1.72 (m, 2H), 4.15 (t, J=6.7 Hz, 2H), 6.25 (d, J=13.4 Hz, 1H), 7.37 (d, J=13.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.03, 22.59, 25.85, 28.52, 29.14 (two peaks), 31.73, 65.05, 124.90, 137.32, 164.10; MS (70 eV) m/z (rel intensity) 183 (M^+−^{35}Cl, 3), 112(18), 109(M^++2−C_8H_{15}, 10), 107 (M^+−C_8H_{15}, 25), 91(M^++2−C_8H_{15}−H_2O, 37), 89 (M^+−C_8H_{15}−H_2O, 100), 70(66), 69(52), 56(69), 55(62), 43(52), 41(63). Found: C, 60.22; H, 8.75%. Calcd for $C_{11}H_{19}ClO_2$: 60.41; H, 8.76%.

Octyl (*Z*)-3-Chloroacrylate: Bp 71—75 °C (0.80 Torr, bath temp); IR (neat) 2952, 2924, 2854, 1732, 1619, 1467, 1349, 1278, 1223, 1168, 809 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.4 Hz, 3H), 1.28 (bs, 10H), 1.58—1.78 (m, 2H), 4.18 (t, J=6.7 Hz, 2H), 6.20 (d, J=8.3 Hz, 1H), 6.70 (d, J=8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.06, 22.63, 25.91, 28.54, 29.16 (two peaks), 31.76, 64.89, 121.56, 132.17, 163.57; MS (70 eV)

m/z (rel intensity) 183 ($M^+-^{35}Cl$, 0.8), 112(11), 109(M^++2−C_8H_{15}, 12), 107 ($M^+-C_8H_{15}$, 34), (M^+−2−$C_8H_{15}-H_2O$, 26), 89($M^+-C_8H_{15}-H_2O$, 92), 70(50), 56(61), 55(62), 43(79), 41(100). Found: C, 60.53; H, 8.95%. Calcd for $C_{11}H_{19}ClO_2$: C, 60.41; H, 8.76%.

Octyl 3-Bromo-3-chloropropanoate (5a): Bp 86—91 °C (1 Torr, bath temp); IR (neat) 2954, 2924, 2854, 1741, 1467, 1350, 1276, 1228, 1183, 1148, 685, 622 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.5 Hz, 3H), 1.28(bs, 10H), 1.56—1.71 (m, 2H), 3.39 (d, *J*=6.8 Hz, 2H), 4.15 (t, *J*=6.7 Hz, 2H), 6.07 (t, *J*=6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.05, 22.59, 25.77, 28.42, 29.10 (two peaks), 31.71, 49.52, 52.87, 65.60, 167.80; MS (70 eV) *m/z* (rel intensity) 191 (M^++4−C_8H_{15}, 0.9), 189 (M^++2−C_8H_{15}, 4.2), 187 ($M^+-C_8H_{15}$, 3.3), 173 (M^++4−$C_8H_{15}-H_2O$, 1.3), 171 (M^++2−$C_8H_{15}-H_2O$, 5.5), 169 ($M^+-C_8H_{15}-H_2O$, 3.6), 143(9), 112(9), 70(61), 56(88), 55(67), 43(87), 42(54), 41(100). Found: C, 44.29; H, 6.83%. Calcd for $C_{11}H_{20}BrClO_2$: C, 44.09; H, 6.73%.

Octyl (*E*)-3-Bromoacrylate (4b): Bp 86—91 °C (2 Torr, bath temp); IR (neat) 2952, 2926, 2854, 1725, 1607, 1297, 1262, 1229, 1153 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.59—1.72 (m, 2H), 4.15 (t, *J*=6.7 Hz, 2H), 6.53 (d, *J*=13.9 Hz, 1H), 7.60 (d, *J*=13.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.03, 22.59, 25.85, 28.52, 29.13 (two peaks), 31.72, 65.12, 126.38, 128.87, 164.10; MS (70 eV) *m/z* (rel intensity) 183 ($M^+-^{79}Br$, 5), 153 (M^++2−C_8H_{15}, 27), 151 ($M^+-C_8H_{15}$, 28), 135 (M^++2−$C_8H_{15}-H_2O$, 90), 133 ($M^+-C_8H_{15}-H_2O$, 94), 112(31), 107(22), 105(22), 84(59), 83(58), 70(100), 69(70), 56(94), 55(86), 43(81), 42(56), 41(96). Found: C, 50.28; H, 7.56%. Calcd for $C_{11}H_{19}BrO_2$: C, 50.20; H, 7.28%.

Octyl (*Z*)-3-Bromoacrylate: Bp 65—70 °C (0.43 Torr, bath temp); IR (neat) 2952, 2924, 2852, 1732, 1614, 1467, 1333, 1208, 1166, 808 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.60—1.75 (m, 2H), 4.18 (t, *J*=6.7 Hz, 2H), 6.63 (d, *J*=8.3 Hz, 1H), 6.99 (d, *J*=8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.03, 22.59, 25.89, 28.49, 29.12 (two peaks), 31.72, 64.93, 120.89, 124.59, 163.99; MS (70 eV) *m/z* (rel intensity) 183 ($M^+-^{79}Br$, 3), 153 (M^++2−C_8H_{15}, 55), 151 ($M^+-C_8H_{15}$, 59), 135 (M^++2−$C_8H_{15}-H_2O$, 87), 133 ($M^+-C_8H_{15}-H_2O$, 87), 112(34), 107(18), 105(21), 84(53), 70(84), 69(62), 56(83), 55(76), 43(75), 42(51), 41(100). Found: C, 50.26; H, 7.32%. Calcd for $C_{11}H_{19}BrO_2$: C, 50.20; H, 7.28%.

Octyl 3,3-Dibromopropanoate (5b): Bp 89—94 °C (1 Torr, bath temp); IR (neat) 2954, 2924, 2852, 1740, 1348, 1276, 1257, 1225, 1147, 637 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.60—1.75 (m, 2H), 3.52 (d, *J*=7.0 Hz, 2H), 4.15 (t, *J*=6.7 Hz, 2H), 5.95 (t, *J*=7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.07, 22.62, 25.81, 28.46, 29.12 (two peaks), 31.74, 36.24, 50.37, 65.66, 168.16; MS (70 eV) *m/z* (rel intensity) 235 (M^++4−C_8H_{15}, 10), 233 (M^++2−C_8H_{15}, 17), 231 ($M^+-C_8H_{15}$, 9), 217 (M^++4−$C_8H_{15}-H_2O$, 8), 215 (M^++2−$C_8H_{15}-H_2O$, 14), 213 ($M^+-C_8H_{15}-H_2O$, 6), 189(10), 187(21), 185(12), 135(18), 133(20), 112(35), 84(78), 83(67), 70(92), 69(63), 57(67), 56(87), 55(85), 43(97), 42(60), 41(100). Found: C, 38.51; H, 5.86%. Calcd for $C_{11}H_{20}Br_2O_2$: C, 38.40; H, 5.86%.

Octyl (*E*)-3-Fluoroacrylate (4c): Bp 74—78 °C (7 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1730, 1662, 1306, 1273, 1133, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.58—1.73 (m, 2H), 4.14 (t, *J*=6.7 Hz, 2H), 5.78 (dd, *J*=14.9, 11.3 Hz, 1H), 7.56 (dd, *J*=79.9, 11.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.05, 22.61, 25.87, 28.54, 29.16 (two peaks), 31.75, 64.83, 106.79 (d, *J*=14.9 Hz), 162.91 (d, *J*=279.8 Hz), 165.33 (d, *J*=22.9 Hz); ^{19}F NMR ($CDCl_3$) δ=−112.22 (dd, *J*=79.7, 14.8 Hz); MS (70 eV) *m/z* (rel intensity) 112(7), 91 ($M^+-C_8H_{15}$, 19), 73 ($M^+-C_8H_{15}-H_2O$, 100). Found: C, 65.26; H, 9.64%. Calcd for $C_{11}H_{19}FO_2$: C, 65.32; H, 9.47%.

Octyl 3-Bromo-3-fluoropropanoate (5c): Bp 74—78 °C (1 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1740, 1328, 1307, 1265, 1231, 1158, 1034, 638 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.58—1.75 (m, 2H), 3.22 (ddd, *J*=23.8, 16.5, 5.1 Hz, 1H), 3.39 (ddd, *J*=16.5, 12.1, 7.0 Hz, 1H), 4.15 (t, *J*=6.7 Hz, 2H), 6.77 (ddd, *J*=49.5, 7.0, 5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.06, 22.61, 25.77, 28.42, 29.12 (two peaks), 31.73, 45.91 (d, *J*=22.8 Hz), 65.65, 88.98 (d, *J*=252.1 Hz), 167.41 (d, *J*=6.9 Hz); ^{19}F NMR ($CDCl_3$) δ=−134.67 (ddd, *J*=49.2, 21.7, 13.8 Hz); MS (70 eV) *m/z* (rel intensity) 173 (M^++2−C_8H_{15}, 3), 171 ($M^+-C_8H_{15}$, 3), 155 (M^++2−$C_8H_{15}-H_2O$, 6), 153 ($M^+-C_8H_{15}-H_2O$, 8), 127(8), 125(10), 112(8), 70(61), 56(83), 55(67), 43(100), 42(54), 41(96). Found: C, 46.95; H, 7.10%. Calcd for $C_{11}H_{20}BrFO_2$: C, 46.66; H, 7.12%.

Octyl (*E*)-3-Iodoacrylate (4d): Bp 89—93 °C (1 Torr, bath temp); IR (neat) 2952, 2924, 2852, 1723, 1592, 1296, 1258, 1214, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.59—1.72 (m, 2H), 4.14 (t, *J*=6.7 Hz, 2H), 6.89 (d, *J*=14.8 Hz, 1H), 7.87 (d, *J*=14.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.05, 22.59, 25.85, 28.51, 29.12 (two peaks), 31.73, 65.12, 99.17, 136.54, 164.20; MS (70 eV) *m/z* (rel intensity) 199 ($M^+-C_8H_{15}$, 47), 181 ($M^+-C_8H_{15}-H_2O$, 100), 153(29), 127(12), 112(25), 70(55), 56(54), 55(52), 43(55), 41(61). Found: C, 42.72; H, 6.39%. Calcd for $C_{11}H_{19}IO_2$: C, 42.60; H, 6.17%.

Octyl (*Z*)-3-Iodoacrylate: Bp 75—80 °C (0.73 Torr, bath temp); IR (neat) 2952, 2922, 2852, 1729, 1600, 1323, 1195, 1164 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.4 Hz, 3H), 1.28 (bs, 10H), 1.62—1.76 (m, 2H), 4.19 (t, *J*=6.7 Hz, 2H), 6.91 (d, *J*=8.9 Hz, 1H), 7.45 (d, *J*=8.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.07, 22.63, 25.94, 28.53, 29.16 (two peaks), 31.76, 65.01, 94.43, 129.99, 164.68; MS (70 eV) *m/z* (rel intensity) 310 (M^+, 2), 199 ($M^+-C_8H_{15}$, 67), 198(92), 181 ($M^+-C_8H_{15}-H_2O$, 100), 153(25), 112(18), 56(50), 43(60), 41(67). Found: C, 42.52; H, 6.17%. Calcd for $C_{11}H_{19}IO_2$: C, 42.60; N, 6.17%.

Octyl 3,3-Diiodopropanoate (5d): Bp 105—109 °C (0.82 Torr, bath temp); IR (neat) 2950, 2922, 2852, 1737, 1342, 1269, 1209, 1134, 1084 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, *J*=6.5 Hz, 3H), 1.28 (bs, 10H), 1.60—1.73 (m, 2H), 3.72 (d, *J*=7.4 Hz, 2H), 4.14 (t, *J*=6.6 Hz, 2H), 5.27 (t, *J*=7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=−43.32, 14.07, 22.61, 25.87, 28.50, 29.12 (two peaks), 31.74, 53.44, 65.56, 169.47; MS (70 eV) *m/z* (rel intensity) 438 (M^+, 2), 311 (M^+−I, 4), 281(10), 199(11), 181(16), 154(13), 113(22), 71(78), 57(100), 43(80). Found: C, 30.39; H, 4.56%. Calcd for $C_{11}H_{20}I_2O_2$: C, 30.16; H, 4.60%.

Methyl (*E*)-3-Chloro-2-hexylacrylate (4e): Bp 62—66 °C (6 Torr, bath temp); IR (neat) 2954, 2926, 2856, 1725, 1608, 1459, 1437, 1338, 1322, 1244, 1196, 1133, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (d, *J*=6.4 Hz, 3H), 1.20—1.55 (m, 8H), 2.41—2.49 (m, 2H), 3.77 (s, 3H), 7.29 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=14.07, 22.55, 27.28, 27.75, 29.05, 31.54, 52.05, 131.92, 135.52, 165.83; MS (70 eV) *m/z* (rel intensity) 175 (M^++2−OMe, 2), 173 (M^+−OMe, 7), 170(6), 169 ($M^+-^{35}Cl$, 49), 136 (M^++2−C_5H_{10}, 10), 134 ($M^+-C_5H_{10}$, 31), 125(14), 121(11), 109(52), 103(20), 43(100), 41(51). Found: C, 58.47; H, 8.35%. Calcd for $C_{10}H_{17}ClO_2$: C, 58.68; H, 8.37%.

Methyl 2-(Bromochloromethyl)octanoate (5e, Diastereo-

meric Mixture (50:50)): Bp 78—83 °C (5 Torr, bath temp); IR (neat) 2952, 2924, 2856, 1741, 1459, 1437, 1356, 1257, 1203, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.4 Hz, 3H), 1.28 (bs, 8H), 1.65—2.02 (m, 2H), 3.07 (ddd, J=9.8, 8.2, 4.0 Hz, 0.50 H), 3.12 (ddd, J=10.0, 8.2, 4.0 Hz, 0.50 H), 3.76 (s, 3H), 5.88 (d, J=8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.01, 22.50, 26.83, 28.89, 30.23, 30.58, 31.46, 52.25, 57.55, 57.78, 59.13, 59.75, 171.19, 171.47; MS (70 eV) m/z (rel intensity) 257 (M^++4−OMe, 1.3), 255 (M^++2−OMe, 5.3), 253 (M^+−OMe, 3.8), 207 (M^++2−^{79}Br, 25), 205 (M^+−^{79}Br, 73), 173(23), 157(20), 123(80), 122(18), 121(100), 109(76), 59(75), 55(73), 43(76), 41(74), 39(52). Found: C, 42.35; H, 6.61%. Calcd for $C_{10}H_{18}BrClO_2$: C, 42.05; H, 6.35%.

Methyl (*E*)-3-Bromo-2-hexylacrylate (4f): Bp 70—74 °C (5 Torr, bath temp); IR (neat) 2954, 2926, 2856, 1724, 1608, 1436, 1293, 1232, 1129 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.25—1.55 (m, 8H), 2.43—2.51 (m, 2H), 3.76 (s, 3H), 7.51 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=14.03, 22.53, 27.62, 29.03, 29.68, 31.51, 52.11, 122.55, 138.30, 165.29; MS (70 eV) m/z (rel intensity) 219 (M^++2−OMe, 4.1), 217 (M^+−OMe 3.5), 180 (M^++2−C_5H_{10}, 15), 178 (M^+−C_5H_{10}, 16), 170(11), 169 (M^+−^{79}Br, 100), 137(16), 109(58), 43(81). Found: C, 48.14; H, 7.06%. Calcd for $C_{10}H_{17}BrO_2$: C, 48.21; H, 6.88%.

Methyl 2-(Dibromomethyl)octanoate (5f): Bp 76—80 °C (1 Torr, bath temp); IR (neat) 2952, 2924, 2854, 1740, 1458, 1435, 1353, 1255, 1212, 1158, 662, 615 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.4 Hz, 3H), 1.29 (bs, 8H), 1.64—2.03 (m, 2H), 3.14 (ddd, J=10.0, 8.3, 3.9 Hz, 1H), 3.76 (s, 3H), 5.80 (d, J=8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.00, 22.49, 26.85, 28.87, 31.29, 31.45, 44.26, 52.25, 57.86, 171.32; MS (70 eV) m/z (rel intensity) 301 (M^++4−OMe, 0.7), 299 (M^++2−OMe, 1.3), 297 (M^+−OMe, 0.7), 251 (M^++2−^{79}Br, 20), 249 (M^+−^{79}Br, 20), 167(92), 165(100), 135(11), 133(11), 109(38), 41(53). Found: C, 36.69; H, 5.76%. Calcd for $C_{10}H_{18}Br_2O_2$: C, 36.39; H, 5.50%.

Methyl (*E*)-3-Fluoro-2-hexylacrylate (4g): Bp 65—69 °C (10 Torr, bath temp); IR (neat) 2954, 2928, 2858, 1730, 1659, 1438, 1284, 1252, 1198, 1149, 1124, 1065 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, J=6.5 Hz, 3H), 1.20—1.52 (m, 8H), 2.30 (td, J=7.3, 2.7 Hz, 2H), 3.75 (s, 3H), 7.53 (d, J=82.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=14.02, 22.54, 23.36 (d, J=2.7 Hz), 28.33, 28.88, 31.50, 51.65, 118.56 (d, J=11.1 Hz), 157.99 (d, J=275.7 Hz), 167.22 (d, J=18.6 Hz); ^{19}F NMR ($CDCl_3$) δ=−117.36 (dt, J=82.7, 3.0 Hz); MS (70 eV) m/z (rel intensity) 157 (M^+−OMe, 4), 125(20), 118 (M^+−C_5H_{10}, 13), 109 (41), 43 (100), 41 (63). Found: C, 63.60; H, 9.29%. Calcd for $C_{10}H_{17}FO_2$: C, 63.81; H, 9.10%.

Methyl 2-(Bromofluoromethyl)octanoate (5g, Diastereomeric Mixture (55:45)): Bp 81—85 °C (7 Torr, bath temp); IR (neat) 2952, 2926, 2856, 1740, 1458, 1437, 1255, 1217, 1164, 1047, 630 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.30 (bs, 8H), 1.65—1.90 (m, 2H), 3.02—3.27 (m, 1H), 3.76 (s, 3H), 6.53 (dd, J=49.8, 7.6 Hz, 0.55H), 6.56 (dd, J=49.2, 7.3 Hz, 0.45H); ^{13}C NMR ($CDCl_3$) δ=13.95, 22.46, 26.51, 26.81, 28.50 (d, J=3.0 Hz), 28.87, 31.41, 52.19, 54.84 (d, J=52.7 Hz), 55.23 (d, J=54.8 Hz), 93.37 (d, J=256.2 Hz), 94.72 (d, J=254.1 Hz), 170.74 (d, J=3.9 Hz), 170.88 (d, J=10.5 Hz); ^{19}F NMR ($CDCl_3$) δ=−134.11 (dd, J=49.2, 9.8 Hz, 0.45F), −141.58 (dd, J=49.2, 10.8 Hz, 0.55F); MS (70 eV) m/z (rel intensity) 189 (M^+−^{79}Br, 25), 157(6), 109(14), 106(5), 105(100). Found: C, 44.92; H, 6.98%. Calcd for $C_{10}H_{18}BrFO_2$: C, 44.62; H, 6.74%.

Dehydrohalogenation of Octyl 3,3-Dihalopropanoates or Methyl 2-(Dihalomethyl)octanoate. The crude product prepared by the reaction of ketene silyl acetal **1a** or **1b** (2.0 mmol) with trihalomethane (1.0 mmol) was treated with Et_3N (2 ml) at room temperature. After stirring for 0.5—1 h, the resulting precipitate was filtered through anhydrous Na_2SO_4. The filtrate was concentrated in vacuo and the residual oil was submitted to silica-gel column chromatography to give octyl (*E*)-3-haloacrylate. Dehydrohalogenation of methyl 2-(dihalomethyl)octanoate, derived from the reaction of **1c** with trihalomethane, was slow at room temperature, thus a mixture of the crude product and Et_3N (5 ml) was refluxed for 1—8 h.

1,1,1-Tribromopropane: The title compound was prepared according to the reported procedure:[8] Bp 88—90 °C (44 Torr); IR (neat) 2980, 2934, 1450, 1097, 1075, 909, 813, 705, 618 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (t, J=7.0 Hz, 3H), 3.02 (q, J=7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=14.18, 44.50, 53.63; MS (70 eV) m/z (rel intensity) 203 (M^++4−^{79}Br, 48), 201 (M^++2−^{79}Br, 100), 199 (M^+−^{79}Br, 52), 121 (M^++2−^{79}Br−H^{79}Br, 55), 119 (M^+−^{79}Br−H^{79}Br, 57), 39(78). Found: C, 13.10; H, 1.87%. Calcd for $C_3H_5Br_3$: C, 12.83; H, 1.79%.

Octyl (*E*)-3-Bromo-2-pentenoate ((*E*)-6): The stereochemistry (*E*) or (*Z*)-**6** was assigned by the chemical shift of allylic protons. Allylic protons of (*E*)-**6** appear at lower field (δ=3.15) compared to those of (*Z*)-**6** (δ=2.62) due to deshield by carbonyl group. Bp 87—91 °C (1 Torr, bath temp); IR (neat) 2952, 2924, 2854, 1721, 1626, 1459, 1342, 1304, 1181, 1104 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.4 Hz, 3H), 1.19 (t, J=7.4 Hz, 3H), 1.28 (bs, 10H), 1.58—1.73 (m, 2H), 3.15 (q, J=7.3 Hz, 2H), 4.10 (t, J=6.7 Hz, 2H), 6.31 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=13.09, 14.06, 22.61, 25.91, 28.54, 29.16 (two peaks), 31.55, 31.75, 64.62, 122.52, 151.66, 164.30; MS (70 eV) m/z (rel intensity) 292 (M^++2, 2.4), 290 (M^+, 2.9), 211 (M^+−^{79}Br, 20), 181(18), 180 (M^++2−C_8H_{15}, 35), 179(16), 178(M^+−C_8H_{15}, 34), 163(38), 161(33), 99(100). Found: C, 53.72; H, 8.12%. Calcd for $C_{13}H_{23}BrO_2$: C, 53.62; H, 7.96%.

Octyl (*Z*)-3-Bromo-2-pentenoate ((*Z*)-6): Bp 94—98 °C (1 Torr, bath temp); IR (neat) 2952, 2924, 2852, 1733, 1637, 1459, 1292, 1246, 1172 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, J=6.5 Hz, 3H), 1.19 (t, J=7.4 Hz, 3H), 1.28 (bs, 10H), 1.60—1.75 (m, 2H), 2.62 (qd, J=7.4, 1.1 Hz, 2H), 4.15 (t, J=6.7 Hz, 2H), 6.30 (t, J=1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.06, 14.03, 22.58, 25.90, 28.52, 29.13 (two peaks), 31.72, 37.02, 64.63, 118.41, 143.32, 164.40; MS (70 eV) m/z (rel intensity) 211 (M^+−^{79}Br, 2), 181 (M^++2−C_8H_{15}, 43), 179 (M^+−C_8H_{15}, 43), 163 (35), 161 (30), 55(54), 53(66), 43(87), 41(100). Found: C, 53.40; H, 8.11%. Calcd for $C_{13}H_{23}BrO_2$: C, 53.62; H, 7.96%.

Octyl 3,3-Dibromopentanoate (7): Bp 111—115 °C (2 Torr, bath temp); IR (neat) 2952, 2926, 2854, 1741, 1342, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, J=6.4 Hz, 3H), 1.23 (t, J=7.1 Hz, 3H), 1.27 (bs, 10H), 1.60—1.74 (m, 2H), 2.63 (q, J=7.1 Hz, 2H), 3.60 (s, 2H), 4.14 (t, J=6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=12.29, 14.06, 22.60, 25.85, 28.45, 29.11 (two peaks), 31.72, 43.02, 53.90, 65.30, 67.41, 167.76; MS (70 eV) m/z (rel intensity) 293 (M^++2−^{79}Br, 0.4), 292 (M^++2−H^{79}Br, 0.4), 291 (M^+−^{79}Br, 0.5), 290 (M^+−H^{79}Br, 0.2), 263 (M^++4−C_8H_{15}, 0.2), 261 (M^++2−C_8H_{15}, 0.6), 259 (M^+−C_8H_{15}, 0.2), 181(24), 179(21), 71(54), 57(90), 43(100), 41(74). Found: C, 42.25; H, 6.76%. Calcd for $C_{13}H_{24}Br_2O_2$: C, 41.96; H, 6.50%.

Ethyl Octyl Fumarate (8): Bp 92—96 °C (2 Torr, bath temp); IR (neat) 2954, 2926, 2854, 1725, 1297, 1260, 1173, 1154, 1033, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, J=6.4 Hz,

3H), 1.25—1.43 (m, 13H), 1.62—1.76 (m, 2H), 4.20 (t, J=6.7 Hz, 2H), 4.27 (q, J=7.1 Hz, 2H), 6.86 (s, 2H); ^{13}C NMR ($CDCl_3$) δ=14.04 (two peaks), 22.58, 25.82, 28.44, 29.11 (two peaks), 31.71, 61.26, 65.44, 133.51, 133.60, 164.94, 165.02; MS (70 eV) m/z (rel intensity) 211 (M^+-OEt, 20), 146(10), 145 ($M^+-C_8H_{15}$, 100), 128(38), 127 ($M^+-C_8H_{15}-H_2O$, 85), 117(57), 112(24), 100(22), 99(52), 70(79), 69(68), 56(77), 55(99), 43(79), 41(83). Found: C, 65.56; H, 9.62%. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44%.

1-Ethyl 4-Octyl 2-Bromosuccinate (9): Bp 102—106 °C (0.71 Torr, bath temp); IR (neat) 2952, 2926, 2854, 1741, 1333, 1302, 1260, 1207, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.3 Hz, 3H), 1.25—1.40 (m, 13H), 1.55—1.70 (m, 2H), 2.98 (dd, J=17.1, 6.3 Hz, 1H), 3.27 (dd, J=17.1, 8.8 Hz, 1H), 4.11 (t, J=6.7 Hz, 2H), 4.26 (q, J=7.2 Hz, 2H), 4.56 (dd, J=8.8, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.85, 14.04, 22.60, 25.78, 28.46, 29.12 (two peaks), 31.73, 38.31, 39.77, 62.25, 65.39, 169.01, 169.66; MS (70 eV) m/z (rel intensity) 227 (M^++2−C_8H_{15}, 4), 225 ($M^+-C_8H_{15}$, 6), 209 (M^++2−$C_8H_{15}-H_2O$, 15), 207 ($M^+-C_8H_{15}-H_2O$, 12), 181(8), 179(9), 57(58), 56(60), 55(74), 43(98), 41(100). Found: C, 50.12; H, 7.58%. Calcd for $C_{14}H_{25}BrO_4$: C, 49.86; H, 7.47%.

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