

Triethylborane Induced Radical Reaction of Ketene Silyl Acetals with Polyhalomethanes. Synthesis of 3,3-Dihalo- and 3-Haloacrylates

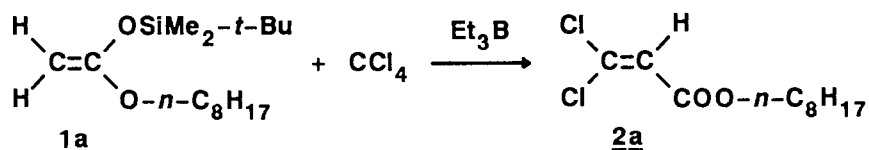
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Treatment of ketene octyl t-butyldimethylsilyl acetal with tetrabromomethane or tribromomethane in the presence of a catalytic amount of triethylborane gave octyl 3,3-dibromoacrylate or octyl (E)-3-bromoacrylate, respectively.

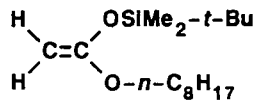
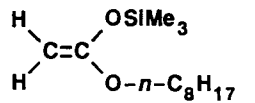
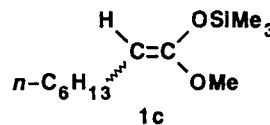
Recently we reported that triethylborane induced a facile addition of perfluoroalkyl iodides to silyl enol ethers to give α -perfluoroalkylated ketones.¹⁾ Here, we report that treatment of ketene silyl acetals with polyhalomethanes gives 3,3-dihalo or 3-haloacrylates in good yields.²⁾

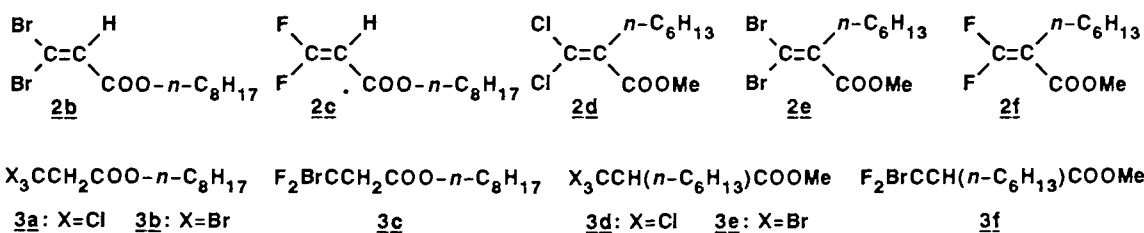
A hexane solution of triethylborane³⁾ (1.0 M, 1 M = 1 mol dm⁻³, 0.2 ml, 0.2 mmol) was added to a solution of ketene octyl t-butyldimethylsilyl acetal **1a** (0.57 g, 2.0 mmol) and tetrachloromethane (0.14 g, 1.0 mmol) in hexane (5 ml) at 25 °C under argon atmosphere. The resulting mixture was stirred for 30 min at 25 °C and saturated aqueous sodium hydrogencarbonate (5 ml) was added. The mixture was stirred for another 30 min and poured into water (20 ml). Extraction with hexane (20 ml x 3) followed by purification by silica-gel column chromatography gave octyl 3,3-dichloroacrylate **2a** (0.24 g) in 95% yield.⁴⁾



The representative results are summarized in Table 1. The reaction of ketene silyl acetals **1a** and **1b** with tetrahalomethanes such as CCl₄, CBrCl₃, CBr₄, and CF₂Br₂ gave 3,3-dihaloacrylates **2** in good yields with an exception of the reaction of **1b** with CF₂Br₂ providing an adduct CF₂CBrCH₂COO-n-C₈H₁₇ **3c** as a major product. On the other hand, ketene silyl acetal **1c** reacted slowly compared with unsubstituted ketene silyl

Table 1. Reaction of Ketene Silyl Acetal with Tetrahalomethane^{a)}

Entry	Ketene silyl acetal	Tetrahalo- methane	Reaction time/h	Product (Yield/% ^{b)})	
				2	3
1	 1a	CCl ₄	0.5	2a (95)	3a (0)
2		CBrCl ₃	0.5	2a (93)	3a (0)
3		CBr ₄	3.0	2b (87)	3b (0)
4		CF ₂ Br ₂	0.5	2c (93)	3c (3)
5	 1b	CCl ₄	0.5	2a (80)	3a (0)
6		CBrCl ₃	0.5	2a (75)	3a (6)
7		CBr ₄	3.0	2b (76)	3b (0)
8		CF ₂ Br ₂	0.5	2c (17)	3c (71)
9	 1c	CCl ₄	12	2d (0)	3d (52)
10		CBrCl ₃	12	2d (0)	3d (90)
11		CBr ₄	12	2e (14)	3e (38)
12		CF ₂ Br ₂	12	2f (0)	3f (73)



a) Ketene silyl acetal (2.0 mmol), tetrahalomethane (1.0 mmol), and Et₃B (0.2 mmol) were employed. b) Isolated yields based on tetrahalomethane.

acetals (**1a** and **1b**) and it took 12 h to give adducts $X_3CCH(n-C_6H_{13})COOMe$ (**3**) as main products. 3,3,3-Trihalopropanoates **3** were easily converted into 3,3-dihaloacrylates upon treatment with base. Thus, treatment of a crude product **3d** with saturated aqueous K₂CO₃ in methanol at 25 °C for 1 h provided **2d** as a single product in 48% yield. Tetrasubstituted ketene silyl acetal Me₂C=C(O-n-C₆H₁₃)OSiMe₃ afforded Cl₃CC(Me₂)COO-n-C₆H₁₃ in 49% yield upon treatment with CBrCl₃ for 12 h.

The reaction of ketene silyl acetals with trihalomethanes has been examined (Table 2). Chloroform did not react with **1a**, **1b**, and **1c**. Meanwhile, the reaction of **1a** or **1b** with CHClBr₂ or CHBr₃ gave the corresponding octyl (E)-3-chloroacrylate **4a** or octyl (E)-3-bromoacrylate **4b** with high stereoselectivity.⁵⁾ In the case of the reaction of **1a** and **1b** with CHFBr₂, octyl 3-bromo-3-fluoropropanoate **5c** was obtained in

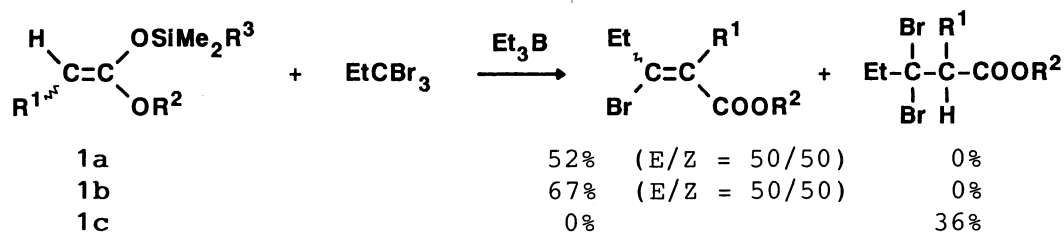
Table 2. Reaction of Ketene Silyl Acetal with Trihalomethane^{a)}

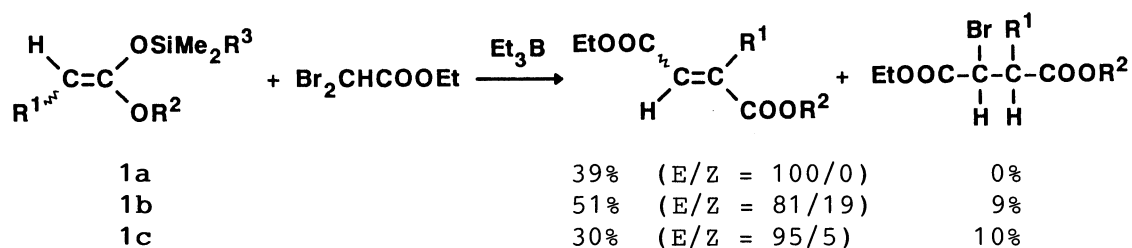
Entry	Ketene silyl acetal	Trihalomethane	Reaction time/h	X	Product (Yield/% ^{b)})	
					4	5
1	1a	CHClBr ₂	1.5	Cl	4a (66)	5a (0)
2	1a	CHBr ₃	1.5	Br	4b (60)	5b (0)
3	1a	CHBrF ₂	1.5	F	4c (14)	5c (34)
4	1b	CHClBr ₂	1.5	Cl	4a (52)	5a (0)
5	1b	CHBr ₃	1.5	Br	4b (66)	5b (0)
6	1b	CHBrF ₂	1.5	F	4c (6)	5c (59)
7	1c	CHClBr ₂	12	Cl	4d (0)	5d (66)
8	1c	CHBr ₃	12	Br	4e (0)	5e (68)
9	1c	CHBrF ₂	12	F	4f (0)	5f (22)

a) Ketene silyl acetal (2.0 mmol), trihalomethane (1.0 mmol), and Et₃B (0.2 mmol) were employed. b) Isolated yields based on trihalomethane.

addition to octyl (E)-3-fluoroacrylate **4c**.⁶⁾ Ketene silyl acetal **1c** provided methyl 2-(dihalomethyl)octanoate **5** as a single product upon treatment with trihalomethanes. 3,3-Dihalopropanoates **5** were easily transformed into 3-haloacrylate derivatives. For instance, the reaction of **1c** with CHBr₃ followed by treatment with Et₃N at 50 °C for 4 h afforded methyl 2-bromomethyleneoctanoate **4e** in 66% yield.

Treatment of **1a**, **1b**, and **1c** with 1,1,1-tribromopropane or ethyl 2,2-dibromopropanoate in the presence of triethylborane catalyst gave the corresponding 3-bromo-2-pentenoate or ethylenedicarboxylate as a (E) and (Z) stereoisomeric mixture as shown below.⁷⁾





References

- 1) K. Miura, M. Taniguchi, K. Nozaki, K. Oshima, and K. Utimoto, *Tetrahedron Lett.*, **31**, 6391 (1990).
- 2) An addition of polyhalomethane to alkenes has been reported. K. Maruoka, H. Sano, Y. Fukutani, and H. Yamamoto, *Chem. Lett.*, **1985**, 1689; H. Matsumoto, T. Nakano, and Y. Nagai, *Tetrahedron Lett.*, **1973**, 5147; J. Tsuji, K. Sato, and H. Nagashima, *Chem. Lett.*, **1981**, 1169; M. Heintz, G. L. Ny and J. Y. Nedelec, *Tetrahedron Lett.*, **25**, 5767 (1984).
- 3) We thank Tosoh Akzo Co. for a gift of a hexane solution of Et₃B.
- 4) Octyl 3,3-dichloroacrylate (**2a**): 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; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) δ 14.00, 22.58, 25.83, 28.44, 29.11 (two peaks), 31.71, 65.16, 120.0, 137.3, 162.3. Found: C, 52.35; H, 7.36%. Calcd for C₁₁H₁₈Cl₂O₂: C, 52.19; H, 7.17%.
- 5) Selective formation of isopropyl (E)-3-fluoroacrylate from isopropyl 3-chloro-3-fluoropropanoate has been reported. H. Malines and C. Wakselman, *J. Fluorine Chem.*, **25**, 447 (1984).
- 6) Octyl (E)-3-fluoroacrylate (**4c**): ¹H NMR (CDCl₃) δ 0.89 (t, J = 4.4 Hz, 3H), 1.15–1.50 (m, 10H), 1.53–1.80 (m, 2H), 4.14 (t, J = 6.7 Hz, 2H), 5.78 (dd, J = 11.4, 14.9 Hz, 1H), 7.55 (dd, J = 11.3, 79.9 Hz, 1H); ¹³C NMR (CDCl₃) δ 14.05, 22.61, 25.87, 28.54, 29.16, 31.75, 64.83, 106.8 (d, J = 14.9 Hz), 162.9 (d, J = 279.8 Hz), 165.3 (d, J = 22.9 Hz).
- 7) The reaction of ketene silyl acetals with Cl₄ or CHI₃ was not so effective as other polyhalomethanes. For instance, treatment of **1a** with Cl₄ or CHI₃ gave I₂C=CHCOO-n-C₈H₁₇ or (E)-C(I)H=CHCOO-n-C₈H₁₇ in 40% or 37% yield, respectively.

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