Highly Efficient Syntheses of Alkyl 3,3-Dialkoxypropanoates, Alkyl 4-Ethoxy-2-oxo-3-butenoates, and Monoprotected Malonaldehydes

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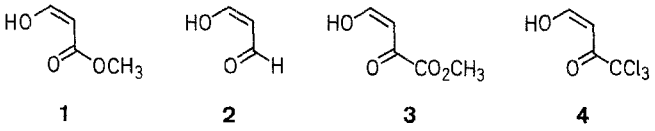
Haloform reaction of 4-alkoxy-1,1,1-trichloro-3-buten-2-ones, which can be obtained by acylation of enol ethers, gives 3,3-dialkoxypropanoic esters. Transacetalization of ethyl 3,3-diethoxypropanoate with 2,2-dimethyl-1,3-propanediol, followed by reduction and oxidation with DMSO/oxalyl chloride yields a monoprotected malonaldehyde. 4-Ethoxy-2-oxo-3-butenoates are synthesized either by acylation of enol ethers with alkoxalyl chlorides or by Claisen condensation of alkyl pyruvates with orthoesters.

Simple 1,3-dicarbonyl compounds like methyl 3-oxopropanoate (**1**), malonaldehyde (**2**), and methyl 4-hydroxy-2-oxobutenoate (methylformylpyruvate, **3**) are versatile intermediates for the synthesis of various products.



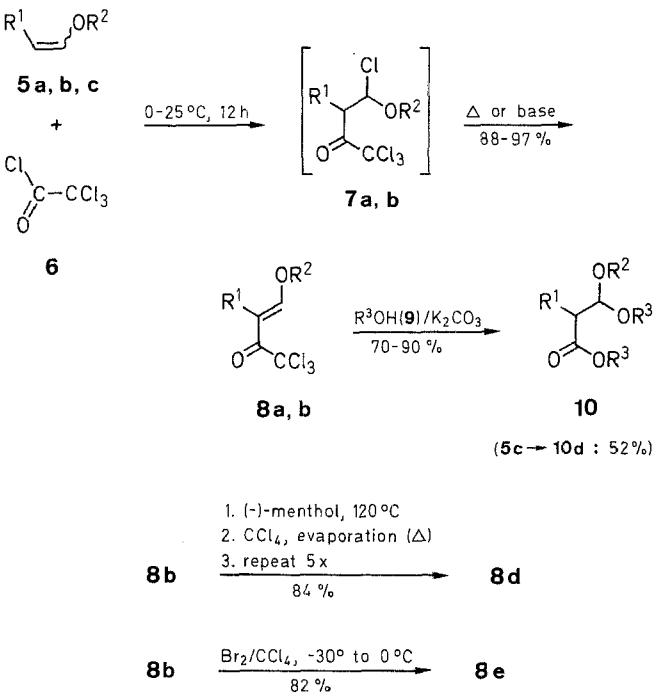
1 **2** **3** **4**

Since these 1,3-dicarbonyl compounds are quite unstable in the free form, their protected derivatives **10, 13**, and **17** are of practical interest. Thus, ethyl 3,3-diethoxypropanoate (**10c**) is a starting material for the preparation of isoxazoles,[1] coumarins,[2] porphyrins,[3] spermines,[4] and uracils.[5,6] In addition, diformylacetates, which are useful educts for the synthesis of 1,4-dihydropyridines[7] and NADH analogs[8] as well as sugar derivatives,[9] can be obtained by formylation of **10a** or **10c**.[10] Monoprotected malonaldehydes such as **13** are valuable educts for the tandem Knoevenagel – hetero-Diels-Alder reaction.[11] 4-Alkoxy-2-oxo-2-butenoic esters such as **17** have been used as enzyme inhibitors[12] and as educts for the synthesis of pyrimidines[13] and benzodiazepines.[14]

We now describe an efficient and simple method for the preparation of compounds of type **10, 13**, and **17**, which can also be performed on a large scale.

The procedure now described for the synthesis of ethyl 3,3-diethoxypropanoate (**10c**) is far superior to the known methods, which afford mixtures of acetals and acrylates,[15] give only moderate yields,[16–18] or require the troublesome use of ketene[19] or expensive ethyl propiolate.[20–22] Other approaches to 3,3-dialkoxypropanoic esters require equipment for electrochemical reactions[23] or palladium(II) catalysis[24] and are only applicable on a small scale.

A known[25] excellent method for the acylation of enol ethers uses activated acyl halides; thus, the reaction of ethyl vinyl ether (**5b**) with trichloroacetyl chloride (**6**) gives the trichloromethyl ketone **8b** in high yield. We have found that **8b** readily undergoes a haloform-type reaction when treated with alcohols **9** in the presence of a catalytic amount of a base to form alkyl 3,3-dialkoxypropanoates **10b** and **10c**, respectively. In a similar manner, methyl 3,3-dimethoxypropanoate (**10a**) could be prepared from **8a**, which is available from methyl vinyl ether **5a** and **6**. Best results in the haloform-type reaction were obtained with potassium carbonate as base. Other bases like 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) can also be used, but complete removal prior to distillation is necessary; otherwise, formation of alkoxyacrylic esters up to 20% can occur. In addition, mixed acetals of the type **10e** can be prepared by heating **8b** with alcohols having a higher boiling point than ethanol, e.g., (−)-menthol, to give the transetherified product (e.g., **8d**) which can then be converted into the mixed acetal (e.g., **10e**) by reaction with an alcohol **9** and potassium carbonate. Further, compound **8b** can be brominated to give 1-bromo-2-ethoxyvinyl trichloromethyl ketone (**8e**).



5	7	8	R^1	R^2	9	R^3
a	a	a	H	CH_3	a	CH_3
b	b	b	H	C_2H_5	b	C_2H_5
c			CH_3	C_2H_5		
		d	H	(−)-menthyl		
		e	Br	C_2H_5		

10	R^1	R^2	R^3
a	H	CH_3	CH_3
b	H	C_2H_5	CH_3
c	H	C_2H_5	C_2H_5
d	CH_3	C_2H_5	C_2H_5
e	H	(−)-menthyl	CH_3
f	Br	C_2H_5	C_2H_5

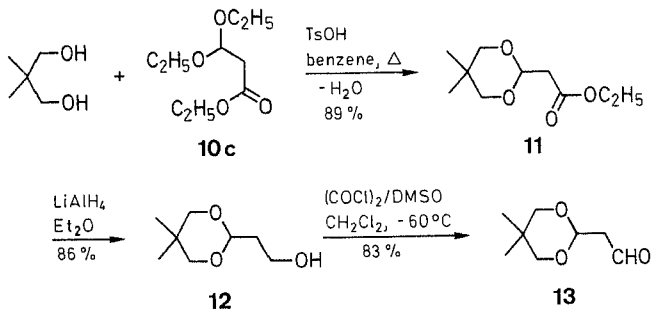
Table 1. Trichloromethyl Ketones **4** and **8** and Alkyl 3,3-Dialkoxypropanoates **10** Prepared

Product	Yield (%)	bp (°C/mbar)	n_D^{20}	IR (film)[a] ν(cm^{-1})	UV (CH_3CN)[b] λ_{max} (nm) (log ε)	^{1}H-NMR ($CDCl_3$/TMS)[c] δ, J(Hz)
4	73	59–61/8	–	3600–2500, 1660, 1585	273 (3.83)	Enol: 6.19 (d, 1H, J = 5.5, 3-H); 7.63 (br d, 1H, J = 5.5, 4-H); 12.5 (br, 1H, OH). Aldehyde: 4.06 (d, 2H, J = 2); 9.83 (t, J = 2, 1-H)
8a	88	102/9.5	1.528	2960, 1710, 1600	269 (4.14)	3.80 (s, 3H); 6.03 (d, 1H, J = 12, 3-H); 7.77 (d, 1H, J = 12, 4-H)
8b	92–97	Lit. [25]	–	–	–	Lit. [25]
8d	84	86–88/0.01 (mp 59–61)	–[d]	2960, 1700, 1605, 1260	280 (4.27)	0.7–2.2 (m, 18H); 3.83 (dt, 1H, J = 4, 11, 1'-H); 6.15 (d, 1H, J = 12, 3-H); 7.80 (d, 1H, J = 12, 4-H)
8e	82	88–90/0.06	–	2995, 1695, 1610	292 (4.00)	1.47 (t, 3H, J = 7.2); 4.40 (q, 2H, J = 7.2); 8.45 (s, 1H, 4-H)
10a	80	66–67/14	1.4095	–	–	Lit. [10]
10b	90	72–73/12	1.4114 (24°C)	2980, 1745, 1130	–	1.18 (t, 3H, J = 7.2); 2.65 (d, 2H, J = 6.0, 2-H); 3.37 (s, 3H); 3.3–3.7 (m, 2H); 3.70 (s, 3H); 4.90 (t, 1H, J = 6.0, 3-H)
10c	87	92–95/14	1.4117	Lit. [21]	–	Lit. [3a,21] (Synthesis: Lit. [3a,6d,21])
10d	52[e]	71–74/6	–	2980, 1730	–	1.0–1.5 (m, 9H); 2.77 (quin, 1H, J = 7.0, 2-H); 3.3–4.0 (m, 6H); 4.16 (d, 1H, J = 7.0, 3-H) (Synthesis: Lit. [18,30])
10e	75	106–108/0.1	–[f]	2960, 1745, 1045	–	0.7–2.2 (m, 19H); 2.65 (m, 2H, 2-H); 3.25 (dt, 0.7H, J = 4.2, 10.5, 1'-H); 3.34 (s, 3H); 3.41 (dt, 0.3H, J = 4.2, 10.5, 1'-H); 3.70 (s, 3H); 4.96 (t, 0.7H, J = 6.0, 3-H); 5.06 (t, 0.3H, J = 6.0, 3-H)
10f	70[g]	103–106/6	1.4458	–	–	(Synthesis: Lit. [29])

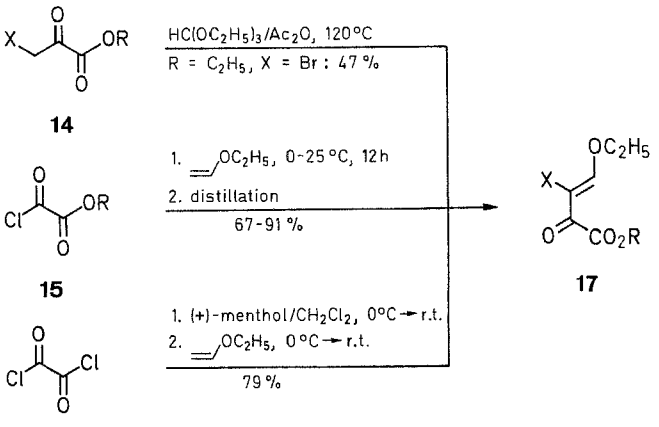
[a] Recorded on a Perkin Elmer 297 spectrometer.
[b] Measured on a Varian Cary 219 UV spectrophotometer.
[c] Obtained on a Varian EM 360 or FT 80 A spectrometer. **10e:** Varian XL 200. **4:** CCl_4 instead of $CDCl_3$.
[d] $[\alpha]_D^{20}$ −52.6° (c = 1, $CHCl_3$).
[e] Yield based on trichloroacetyl chloride.
[f] $[\alpha]_D^{20}$ −76.5° (c = 1, $CHCl_3$); ratio of isomers: 2.4 : 1.
[g] Obtained as a 1 : 1-mixture of **10f** and ethyl 2-bromo-3-ethoxyacrylate.

Acid hydrolysis of **8b** with formic acid leads to the previously unknown free 4,4,4-trichloro-3-oxobutanol(trichloroacetylacetaldehyde, **4**) which can be stored at −20°C for at least two months. In tetrachloromethane, compound **4** shows 96% enolization as indicated by ^{1}H-NMR analysis.

Ethyl 3,3-diethoxypropanoate **(10c)** is a suitable educt for the preparation of monoprotected malonaldehydes. Thus, transacetalization of **10c** with 2,2-dimethyl-1,3-propanediol, reduction of the ester **11** with lithium aluminium hydride, and Swern[26] oxidation of the primary alcohol **12** with dimethyl sulfoxide/oxalyl chloride led to aldehyde **13**[11] in good overall yield.[27]



Finally, stable derivatives of formylpyruvic acid esters such as **17a–c** can also be conveniently obtained. As an extension of reported work[25] we treated methyl, ethyl, and (+)-menthyl chlorooxoacetate **(15a, b**; and crude **15c** obtained from **16)** with ethyl vinyl ether at 0°C and isolated products **17a, b, c** in 91, 67, and 79% yield, respectively. In contrast, the known Claisen condensation of methyl and ethyl pyruvate **(14a, b)** with triethyl orthoformate gave **17a** and **17b** only in 35 and 18% yield, respectively.[12,13,28] Using the latter method we obtained the new bromo compound **17d** in 47% yield.



17	R	X	from	Yield (%)
a	CH_3	H	**14**	35[12,13]
			15	67
b	C_2H_5	H	**14**	18[28]
			15	91
c	(+)-menthyl	H	**16**	79
d	C_2H_5	Br	**14**	47

1,1,1-Trichloro-4-methoxy-3-buten-2-one (8a):
A vigorously stirred mixture of trichloroacetyl chloride (270 g, 1.48 mol) and dry pyridine (117 g, 1.48 mol) is cooled under N_2 to −10°C. An efficient reflux condenser (kept at −20°C by a cryostat) is used. Methyl vinyl ether (145 mL, 1.9 mol) is added and stirring is continued for 12 h at 0°C. Then, H_2O (200 mL) is added and the mixture is extracted with Et_2O (2 × 200 mL). The organic extract is dried (Na_2SO_4), and distilled through a short Vigreux column to give **8a**; yield: 265 g (88%); bp 102°C/9.5 mbar; n_D^{20} 1.5238.

$C_5H_5Cl_3O_2$ (203.5) calc. C 29.52 H 2.48 Cl 52.28
found 29.60 2.44 52.05

Table 2. Alkyl 4-Ethoxy-2-oxo-3-butenoates **17** Prepared

Product	Yield (%)	bp (°C/mbar)	MS (70 eV)[a] *m/z* (%)	IR (film)[b] ν (cm^{-1})	UV (CH_3CN)[c] λ_{max} (nm) (log ε)	^{1}H-NMR ($CDCl_3$/TMS)[d] δ, *J* (Hz)
17a	67	123–126/14	–	2990, 1735, 1610, 1590	276 (4.01)	1.37 (t, 3H, *J* = 7.0); 3.85 (s, 3H); 4.10 (q, *J* = 7.0, 2H); 6.13 (d, 1H, *J* = 12.4, 3-H); 7.88 (d, 1H, *J* = 12.4, 4-H)
17b	91	89–90/0.6	Lit. [12]	Lit. [27]	Lit. [12]	Lit. [12]
17c[e]	79[f]	138–142/0.006	282 (0.2, M^+), 238 (0.4, $M - CO_2$), 99 (100)	2960, 1720, 1610, 1590	276 (3.93)	0.7–2.4 (m, 21H); 4.03 (q, 2H, *J* = 7.0); 4.80 (dt, 1H, *J* = 4.5, 10.0, 1'-H); 6.10 (d, 1H, *J* = 12.5, 3-H); 7.78 (d, 1H, *J* = 12.5, 4-H)
17d	47	115–118/0.06	250 (20, M^+), 177 (100, $M - CO_2C_2H_5$)	2950, 1730, 1670, 1605	275 (4.07)	1.37 (t, 3H, *J* = 7.0); 1.43 (t, 3H, *J* = 7.0); 4.35 (q, 2H, *J* = 7.0); 4.38 (q, 2H, *J* = 7.0); 8.32 (s, 1H, 4-H)

[a] Recorded on a Varian MAT 311 A spectrometer.
[b] Recorded on a Perkin Elmer 297 spectrometer.
[c] Measured on a Varian Cary 219 UV spectrophotometer.
[d] Obtained on a Varian EM 360 or FT 80 A spectrometer.
[e] $[\alpha]_D^{20} + 77.9°$ ($c = 1$, $CHCl_3$).
[f] Yield based on oxalyl chloride.

4,4,4-Trichloro-3-oxobutanal (4):
A solution of 1,1,1-trichloro-4-ethoxy-3-buten-2-one[31] (**8b**; 10.9 g, 50.0 mmol) in formic acid (100 g) is stirred for 20 h, then extracted with petroleum ether (5 × 40 mL), the acid layer being saved. The organic extract is washed with H_2O (50 mL) and with saturated NaCl solution (50 mL), dried (Na_2SO_4), and concentrated under reduced pressure to give 8.3 g of crude product. Dilution of the acid layer with H_2O (300 mL), extraction with Et_2O (3 × 40 mL) and further proceeding as above affords an additional 0.5 g of product. Distillation of the combined product *in vacuo* affords **4**; yield: 6.9 g (73%); bp 59–61°C/8 mbar.

$C_4H_3Cl_3O_2$	calc.	C 25.36	H 1.60	Cl 56.15
(189.4)	found	25.41	1.60	56.09

1,1,1-Trichloro-4-(−)menthyloxy-3-buten-2-one (8d):
A mixture of (−)-menthol (7.00 g, 44.8 mmol) and 1,1,1-trichloro-4-ethoxy-3-buten-2-one (**8b**, 9.74 g, 44.8 mmol) is kept at 120°C. CCl_4 (10 mL) is added, and volatile compounds are distilled off through a short Vigreux column. This procedure is repeated five times until only traces of **8b** are detected by TLC on silica gel (*t*-BuOMe/petroleum ether 1:10; **8b**: R_f 0.43, **8d**: R_f 0.69). Distillation *in vacuo* affords **8d**; yield: 12.3 g (84%); bp 86–88°C/0.01 mbar; mp 59–61°C.

$C_{14}H_{21}Cl_3O_2$	calc.	C 51.32	H 6.46	Cl 32.46
(327.7)	found	51.51	6.54	32.29

3-Bromo-1,1,1-trichloro-4-ethoxy-3-buten-2-one (8e):
To a solution of 1,1,1-trichloro-4-ethoxy-3-buten-2-one (**8b**; 72.5 g, 0.33 mol) and CCl_4 (90 mL) under N_2, a solution of Br_2 (53.5 g, 0.34 mol) in CCl_4 (60 mL) is added dropwise at −30°C over 60 min. The mixture is diluted with CH_2Cl_2 (200 mL) and Et_3N (50 mL) is added at 0°C with vigorous stirring. The ammonium salts are then filtered off and carefully washed with Et_2O. Removal of solvents and distillation affords the crude product **8e**; yield: 90 g (91%); bp 102–110°C/0.2 mbar. Careful redistillation gives pure **8e**; yield: 80.5 g (82%); bp 98–100°C/0.1 mbar.

$C_6H_6BrCl_3O_2$	calc.	C 24.31	H 2.04	
(296.4)	found	24.43	2.07	

Methyl (±)-3-Ethoxy-3-methoxypropanoate (10b); Typical Procedure:
To a stirred mixture of K_2CO_3 (19 g, 10 mol%) and dry MeOH (200 mL), 1,1,1-trichloro-4-ethoxy-3-buten-2-one (**8b**; 300 g, 1.38 mol) is added dropwise within 30 min with cooling in a water bath and stirring is continued for 10 h at room temperature. Petroleum ether (200 mL) is then added, K_2CO_3 is filtered off, and the filtrate is concentrated under reduced pressure. If K_2CO_3 precipitates during the concentration, the above procedure must be repeated. Distillation *in vacuo* affords **10b**; yield: 203 g (91%); bp 72–73°C/12 mbar; n_D^{24} 1.4114.

$C_7H_{14}O_4$	calc.	C 51.84	H 8.70	
(162.2)	found	52.06	8.70	

Methyl 3-(−)-Menthyloxy-3-methoxypropanoate (10e):
Method A: Potassium carbonate (0.5 g) is added to a stirred solution of 1,1,1-trichloro-4-(−)-menthyloxy-3-buten-2-one (**8d**; 9.00 g, 27.5 mmol) in MeOH (120 mL). A slightly yellow coloration appears. Stirring is continued for 14 h at room temperature, the solvent removed and the residue distillated *in vacuo* to afford **10e** containing 20% of ethyl 3-(−)-menthyloxyacrylate; yield: 5.81 g (78%); bp 106–108°C/0.1 mbar; ratio of diastereoisomers of **10da**: 2.4:1.

Method B: 1,1,1-Trichloro-4-(−)-menthyloxy-3-buten-2-one (**8d**; 1.58 g, 4.82 mmol) is added to a stirred solution of MeONa [prepared from Na (0.15 g) and MeOH (40 mL). Stirring is continued for 1 h and the mixture then poured into H_2O (200 mL). The resultant mixture is extracted with *t*-BuOMe/petroleum ether (1:1; 5 × 100 mL), the extract is dried (Na_2SO_4), the solvent is evaporated, and the residue purified by column chromatography on silica gel using *t*-BuOMe/hexane (1:20) as eluent to give **10e**; yield: 0.99 g (75%); R_f 0.31. R_f of accompanying ethyl 3-(−)-menthyloxyacrylate: 0.38.

$C_{15}H_{28}O_4$	calc.	C 66.14	H 10.35	
(272.4)	found	66.21	10.33	

Ethyl (±)-3,3-Diethoxy-2-methylpropanoate (10d):
Propenyl ethyl ether (**5c**; 96.0 g, 1.12 mol) is added dropwise, with stirring at 0°C, within 30 min to trichloroacetyl chloride (**6**; 135 g, 0.743 mol) under N_2. The mixture is allowed to warm to room temperature within 3 h, stirring is continued for 10 h, and the mixture is then added to a solution of EtONa [prepared from Na (23 g, 1.0 mol) and EtOH (300 mL] with vigorous stirring at 0°C. A persisting yellow color indicates an andequate excess of EtONa whereas a greyish brown tinge indicates a surplus of haloether; in the latter case, small pieces of sodium are added until the yellow color appears. The mixture is hydrolyzed with H_2O (200 mL) and extracted with Et_2O (3 × 100 mL). The extract is dried (Na_2SO_4) and the residue distilled *in vacuo* to give **10d**; yield: 78.8 g (52%); bp 71–74°C/8 mbar (Lit.[18] bp 99–102°C/27 mbar).

5,5-Dimethyl-1,3-dioxan-2-acetaldehyde (13):
Ethyl 5,5-Dimethyl-1,3-dioxan-2-acetate (**11**): A mixture of ethyl 3,3-diethoxypropanoate (**10c**; 9.5 g, 50 mmol), 2,2-dimethylpropane-1,3-diol (5.2 g, 50 mmol), 4-toluenesulfonic acid hydrate (100 mg), and benzene (100 mL) is heated and the azeotrope formed (benzene/EtOH) is allowed to distil off through a column. When the boiling point of the distillate reaches 80°C, the residue is cooled, neutralized with solid $NaHCO_3$, and distilled to give ester **11**; yield: 9.0 g (89%); bp 86–93°C/3–5 mbar.

$C_{10}H_{18}O_4$	calc.	C 59.39	H 8.97	
(202.3)	found	59.22	9.01	

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.72 (s, 3H, 5'-CH_3); 1.17 (s, 3H, 5'-CH_3); 1.25 (t, 3H, *J* = 7 Hz, OCH_2CH_3); 2.66 (d, 2H, *J* = 5.5 Hz, 2-H); 3.3–3.8 (m, 4H, 4'-H, 6'-H); 4.15 (q, 2H, *J* = 7 Hz), OCH_2CH_3); 4.84 (t, 1H, *J* = 5.5 Hz, 2'-H).

5,5-Dimethyl-1,3-dioxan-2-ethanol (**12**): A stirred mixture of $LiAlH_4$ (1.00 g, 25 mmol) and Et_2O (30 mL) is kept at reflux by the dropwise addition of ester **11** (8.50 g, 42 mmol). Stirring is continued for 5 min. excess hydride is hydrolyzed with H_2O, and 5N H_2SO_4 is added to dissolve the formed aluminate. The aqueous layer is extracted with CH_2Cl_2 (3 × 50 mL) the combined organic layer and extract is dried (Na_2SO_4), evaporated and distilled to afford alcohol **12**; yield: 5.75 g (86%); bp 65–68 °C/0.7–0.8 mbar.

$C_8H_{16}O_3$	calc.	C 59.98	H 10.07
(160.2)	found	59.72	10.19

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.73 (s, 3H, 5'-CH_3); 1.20 (s, 3H, 5'-CH_3); 1.91 (dt, 2H, J = 6, 5.5 Hz, 2-H); 2.83 (s, 1H, D_2O exchangeable, OH); 3.3–3.8 (m, 4H, 4'-H, 6'-H); 3.77 (t, 2H, J = 5.5 Hz, 1-H); 4.65 (t, 1H, J = 6 Hz, 2'-H).

5,5-Dimethyl-1,3-dioxan-2-acetaldehyde (**13**) : To a stirred and cooled (– 60 °C) solution of oxalyl chloride (4.80 g, 3.25 mL, 35.0 mmol) in CH_2Cl_2 (80 mL) under N_2, DMSO (5.9 mL) is added dropwise within 15 min and stirring is continued for 10 min. Then, a solution of alcohol **12** (5.50 g, 34.4 mmol) in CH_2Cl_2 (35 mL) is added. The mixture is stirred for 15 min and Et_3N (15.2 g, 150 mmol) is added over ~ 5 min with stirring at – 60 °C. The mixture is allowed to warm to room temperature, hydrolyzed with H_2O (100 mL), and extracted with CH_2Cl_2 (3 × 30 mL). After washing with H_2O (30 mL) and brine (30 mL) and drying (Na_2SO_4), solid $NaHCO_3$ (~ 0.5 g) is added to the extract and this mixture is distilled, first at ambient pressure, then under vacuum to give aldehyde **13** contaminated by traces of DMSO; yield: 5.05 g. For removal of this impurity the distillate is dissolved in a mixture of Et_2O and petroleum ether (2:1, 50 mL); the obtained solution is washed with H_2O (25 mL) and brine (25 mL) and dried (Na_2SO_4). The solvent is evaporated at atmospheric pressure. Distillation of the residue gives sufficiently pure **13**; yield: 4.51 g (83%); bp 77–87 °C/8.5 mbar; purity: 97% (GLC).

^{1}H-NMR ($CDCl_3$/TMS): δ = 0.73 (s, 3H, 5'-CH_3); 1.19 (s, 3H, 5'-CH_3); 2.68 (dd, 2H, J = 5, 2.5 Hz, 2-H); 3.3–3.8 (m, 4H, 4'-H, 6'-H); 9.81 (t, 1H, J = 2.5 Hz, 1-H).

2,4-DNP of **13**: mp 150–151 °C (EtOH).

$C_{14}H_{18}N_4O_6$	calc.	C 49.70	H 5.36	N 16.56
(338.3)	found	49.72	5.28	16.60

Ethyl 4-Ethoxy-2-oxo-3-butenoate (17b):
Ethyl vinyl ether (13.0 g, 180 mmol) is added dropwise under N_2 at 0 °C and with stirring to ethyl chlorooxoacetate (**15**, R = C_2H_5; 10.0 mL, 90.0 mmol) within 20 min. Cooling is maintained for at least 2 h. The mixture is then allowed to gradually warm to room temperature within 15 h, and distilled *in vacuo*, yield: 14.1 g (91%) of **17b** as a pale yellow liquid; bp 89–90 °C/0.6 mbar (Lit.[27] bp 135–138/14 mbar).

Methyl 4-Ethoxy-2-oxo-3-butenoate (17a):
Prepared in the same way as **17b** from ethyl vinyl ether (80.7 g, 1.12 mol) and methyl chlorooxoacetate (**15**, R = CH_3; 68.0 g, 0.56 mol); yield: 58.9 g (67%); solidification occurs in the refrigerator; mp ~ 12 °C; bp 123–126 °C/14 mbar (Lit.[13] bp 70 °C/0.001 mbar).

(+)-Menthyl 4-Ethoxy-2-oxo-3-butenoate (17c):
A stirred solution of oxalyl chloride (8.0 g, 5.5 mL, 63 mmol) in CH_2Cl_2 (15 mL) is cooled to 0 °C under N_2, (+)-menthol (4.92 g, 31.4 mmol) is added in small portions, and stirring is continued for 1 h at 0 °C and for 5 h at room temperature. Dichloromethane and excess oxalyl chloride are distilled off at a bath temperature of 80 °C. The residue is cooled with an ice bath, ethyl vinyl ether (5 mL) is added, and stirring is continued for 12 h allowing the mixture to warm to room temperature. It is then diluted with dry Et_2O (25 mL), Et_3N (10 mL) is added dropwise at 0 °C, and the formed ammonium salts are filtered off. Distillation of the concentrated filtrate affords **17c** as a slightly yellow oil; yield: 7.02 g (79%); bp 134–142 °C/0.006 mbar.

$C_{16}H_{26}O_4$	calc.	C 68.06	H 9.28
(282.4)	found	67.87	9.61

Ethyl 3-Bromo-4-ethoxy-3-butenoate (17d):
In a distillation apparatus which allows continuous removal of the distillate through a short column, ethyl bromopyruvate (**14**, R = C_2H_5, X = Br; 36.6 g, 0.358 mol), Ac_2O (36.6 g, 0.358 mol), and triethyl orthoformate (35.6 g, 0.219 mol) are heated at 120 °C for 12 h. The temperature is raised to 140 °C within 12 h and maintained at 145 °C for 2 h. Careful fractional distillation *in vacuo* affords **17d**; yield: 15.8 g (47%); bp 115–117 °C/0.06 mbar.

$C_8H_{11}BrO_4$	calc	C 38.27	H 4.42	Br 31.82
(251.1)	found	37.92	4.52	32.20

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