Acyloxylation of 1-Methoxycyclohex-1-ene and Other Enol Ethers with Dimethyl Peroxydicarbonate

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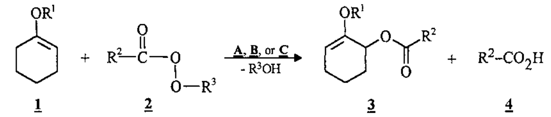
Dedicated to Professor Manfred Regitz on the occasion of his 60th birthday

Acyloxylation of different types of enol ethers (derived from aldehydes and ketones) by dimethyl peroxydicarbonate (DPDC) results in either addition to the double bond or in a formal replacement of an allylic hydrogen by a methoxycarbonyloxy group forming vicinal oxygenated hydrocarbons. 1,3-Oxygenated products via monoacyloxylation could not be observed. The results are compared with copper(I)-catalyzed acyloxylations of 1-methoxycyclohex-1-ene (**1a**) by means of *tert*-butyl peroxycarboxylates **2a**, **b**.

Allylic hydrogens in alkenes are easily replaced by bromine via a S_R reaction using *N*-bromosuccinimide (NBS).[1] Corresponding replacement of allylic hydrogen by acyloxy groups occurs with *tert*-butyl peroxycarboxylates **2** in the presence of copper(I) salts as electron-transfer catalysts (ETC)[2] in the Kharasch–Sosnovsky reaction.[3] Whereas 1-halocycloalk-1-enes react with NBS via S_R yielding 1,3-disubstitution products,[4] the related 1-alkoxycycloalk-1-enes give 1,2-disubstitution (or addition) products.[5] In order to investigate whether the latter compounds would form 1,2- or 1,3-substitution products, 1-methoxycyclohex-1-ene (**1a**) was acyloxylated with *tert*-butyl peracetate (**2a**) and with *tert*-butyl perbenzoate (**2b**). Apart from the poor reactivity of both peresters only minor amounts of vicinal acyloxylation products (**3a**: 11%, **3b** 15%) were formed. The corresponding free carboxylic acids **4** were the main products.[6] The low yields of desired **3a, b** could not be enhanced in the presence of bases (potassium *tert*-butoxide or calcium hydride). Therefore, dimethyl peroxydicarbonate (DPDC)[7] was utilized as acyloxylating agent because elimination of methyl monocarbonate (**4c**) instead of a carboxylic acid would lead subsequently to carbon dioxide and methanol. Additionally, higher reactivity of **2c** compared to **2a, b** (as a consequence of a particularly low *O,O*-bond dissociation energy (BDE)[8]) does not require copper(I) catalysis,[9] while enol ethers as electron-rich olefins react spontaneously with **2c**[10] (Scheme 1).



1	a	b
R^1	CH_3	$SiMe_3$

2	a	b	c
R^2	CH_3	C_6H_5	OCH_3
R^3	t-Bu	t-Bu	CO_2CH_3

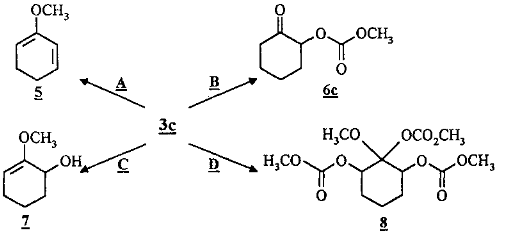
A: neat [CuBr], 70°C, 24-30 h
B: CH_2Cl_2 refl., 30 min
C: CH_2Cl_2 refl., 14 h

3	R^1	R^2	method	[%]
a	CH_3	CH_3	A	11
b	CH_3	C_6H_5	A	15
c	CH_3	OCH_3	B	91
d	$SiMe_3$	OCH_3	C	65

4	R^2	method	[%]
a	CH_3	A	80
b	C_6H_5	A	70
c	OCH_3	B	/

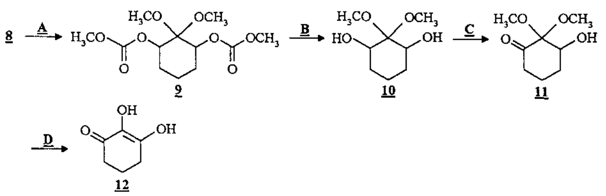
Scheme 1

Since enol silyl ethers have been successfully acyloxylated by means of lead(IV) carboxylates,[11] the reactivity of **1b** toward **2c** as compared to **1a** was checked. The reaction rate was shown to be markedly slower.[12] However, compound **3c** proved to be a rather attractive starting material for further conversions. Subsequent products were obtained via different standard methods: Thermolysis (280 °C, metal bath) led to 2-methoxycyclohexa-1,3-diene (**5**), acid hydrolysis led to 2-(methoxycarbonyloxy)cyclohexanone (**6c**), alkaline saponification led to 2-methoxycyclohex-2-en-1-ol (**7**), and a second conversion with **2c** caused addition to the double bond with formation of **8** (Scheme 2). For structural proof, **7** was hydrolyzed with dilute mineral acid yielding the dimer of 2-hydroxycyclohexanone or was derivatized using a benzoyl chloride/pyridine mixture yielding **3b**; furthermore, **8** has been utilized as the primary product of a new synthesis for 2-hydroxycyclohexa-1,3-dione (**12**) (Scheme 3). Compound **12** was not isolated directly, the characteristic reducing properties have been confirmed qualitatively via positive iron(III) chloride and Tillmans tests,[13] for quantitative determination highly water soluble **12** was precipitated by lead(II) acetate as its insoluble lead(II) complex.[13]



A: 280°C, 86%; B: H_3O^+, 72%; C: KOH/CH_3OH, 76%; D: 3c, CH_2Cl_2 refl., 60%

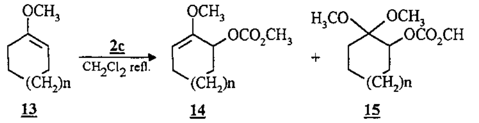
Scheme 2



A: CH_2Cl_2/CH_3OH, 98%; B: KOH/H_2O, CH_3OH, 50°C, 92%; C: PCC, CH_2Cl_2, 61%; D: H_3O^+, 80°C, 75%

Scheme 3

In order to gain more insight into enol ether–DPDC reactions, various enol ethers have been subjected to this acyloxylation procedure. Ketone enol ethers **13a–c** (homologous to **1a**) did not lead to exclusive formation of acyloxylated enol ethers **14** as in the case of **1a**. Methanol formed during the reactions was added in part (**15a, c**) or completely (**15b**) to the double bond yielding acyloxylated cycloalkanone dimethyl acetals **15a–c** (Scheme 4). Pure enol ethers **14b, c** could be finally obtained from their corresponding acetals **15b, c** by diphenylphosphinic acid catalyzed elimination of methanol at 140 °C whereas **15a** suffered resinification under these conditions. Further acyloxylations of **14a–c** were possible; however, these conversions led to crude mixtures of stereomers and other products. Vinyl and vinylene ethers **16–18** (i.e. enol ethers from aldehydes) suffered exclusive addition of **2c** to their double bonds yielding **19–21**. Compounds **20, 21** were obtained as mixtures of diastereomers (Scheme 5).



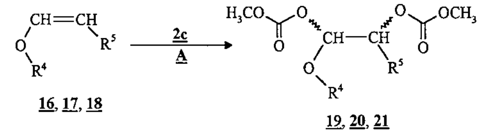
13, 14, 15	a	b	c
n	2	4	5

14 + 15	[%]	ratio 14:15
a	55*)	57 : 43
b	63**)	0 : 100
c	81	65 : 35

*) large amounts of polymeric by-products

**) 3% bis-acyloxylation product in analogy to 8 during 1:1 conversion

Scheme 4



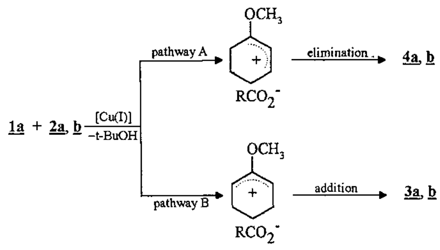
	R^4	R^5
16, 19	i-C$_4$H$_9$	H
17, 20	–(CH$_2$)$_2$–	
18, 21	–(CH$_2$)$_3$–	

	[%]	ratio of diastereomers
19	78*)	/
20	63	55 : 45
21	43	50 : 50

A: CH$_2$Cl$_2$, bath of 50°C, 36 h; *) a bath of 70-80°C gave rise to 57% methoxycarbonyloxyacetaldehyde i-butyl methyl acetal instead of 19

Scheme 5

It is suggested that formation of carboxylic acids **4** as elimination products and formation of desired enol ethers **3** as substitution products of acyloxylations of **1a** by **2a, b** under Kharasch–Sosnovsky conditions are due to the interediacy of two different isomeric methoxy allylic cations (Scheme 6). Pathway A would account for the Kharasch–Sosnovsky mechanism[3,14] i.e. a radical hydrogen abstraction in the first step would be followed by oxidation of the resulting 1-methoxyallyl radical to its cation by copper(II), except that the last step would be an elimination of carboxylic acids **4** instead of ester formation via carboxylate addition. The first step of pathway B is suggested to be the consequence of an one-electron oxidation of electron-rich enol ether **1a** to its cation radical (cf. olefin radical cation formations[15]) followed by deprotonation to give a 2-methoxyallyl radical which is oxidized to its cation. The higher oxidizing power of DPDC compared with peresters **2a, b** was obviously sufficient to cause an uncatalyzed single electron transfer (SET)[16] with enol ethers, therefore reactions of **1a, b** with **2c** should follow pathway B even without copper(I) catalysis (addition of copper(I) salt neither influenced the course nor the rate of the reaction). Since aldehyde enol ethers **16–18** are unable to form 2-alkoxyallyl cations they suffer direct addition of **2c** to the double bond.[17]



Scheme 6

Melting points were determined by means of a Fus-O-mat (Heraeus) or a copper block, IR spectra were recorded on a Beckman IR-33 (films or KBr pellets), NMR spectra were recorded on Varian EM360, Bruker WP80 or AM400 spectrometers (solutions in CDCl$_3$ with TMS as internal standard), elemental analyses were obtained from a Carlo Erba analyzer. TLC control of reaction mixtures were carried out using foils Alugram® SIL G/UV$_{254}$ from Macherey and Nagel. The following compounds are prepared according to known procedures: 1-Methoxycycloalk-1-enes **1a**, **13a–c**,[18] in particular **1a**,[19] 1-trimethylsiloxycyclohex-1-ene (**1b**),[20] dimethyl peroxydicarbonate (**2c**).[21] Other reagents used are commercially available. *tert*-Butyl peroxyesters **2a, b** were dried prior to use according to a known procedure.[22]

Caution: All handling with peroxy compounds were carried out behind a safety shield in a hood. Concentration of reaction mixtures was carried out only after decomposition of unreacted peroxide by boiling with CuCl. No explosions were observed following this procedure.

Satisfactory microanalyses obtained for all new compounds: C ± 0.29, H ± 0.16.

Acyloxylations of 1a with 2 Under Kharasch–Sosnovsky Conditions; General Procedure:

1-Methoxycyclohex-1-ene (**1a**) (for **2a**: 56 g, 0.5 mol or for **2b**: 136 g, 1.2 mol) and a catalytic amount of CuBr (0.5 g or 2 g) were stirred and heated to 70 °C under N$_2$ atmosphere. *tert*-Butyl peracetate (**2a**) (30 g, 0.23 mol) or *tert*-butyl perbenzoate (**2b**) (97 g, 0.5 mol) was added dropwise, and stirring was continued at 70 °C until the deep blue color disappeared (ca. 44 h or 30 h). The cooled reaction mixture was diluted with twice its volume of Et$_2$O, copper salts were removed by filtration, and the AcOH or PhCO$_2$H formed was extracted with aq K$_2$CO$_3$ and determined acidimetrically (80 or 70 %). The organic layer was dried (MgSO$_4$) and evaporated to afford the product **3a** or **3b**.

Hydrolysis of **3b** by refluxing a CH$_2$Cl$_2$ solution with 6 N aq HCl for 2 h afforded 2-benzoyloxycyclohexanone; yield: 82 %; mp 84 °C (Lit.[23] mp 82–84 °C).

Mono- and Bisacyloxylation of 1a with DPDC (2c) and Subsequent Conversions of the Resulting Reaction Products:

(a) *Preparation of a Solution of* **2c**:[24] H$_2$O (200 mL) was added to a mixture of methyl chloroformate (37.8 g, 0.4 mol) and CH$_2$Cl$_2$ (300 mL) in a 2 L beaker. After cooling to 5 °C (ice bath) Na$_2$O$_2$ (17.2 g, 0.22 mol) was added in small portions under vigorous mechanical stirring maintaining the temperature below 10 °C. Stirring was continued for 2 h under further cooling, and the two liquid phases were separated. The organic phase was washed with ice water and dried (K$_2$CO$_3$) at 0 °C for 2 h. Iodometric titration of an aliquot part indicated a yield of ca. 66 % (20 g, 0.14 mol) of **2c**.

Table 1. Enol Ethers **3a–d** Prepared

Product	Yield (%)	bp (°C)/Torr	IR (neat) ν (cm^{-1})	^{1}H NMR (CDCl$_3$/TMS)
3a	11	62/0.001	1625 (C=C), 1740 (C=O)	1.9 (m, 6H, 3×CH$_2$), 2.1 (s, 3H, CH$_3$CO), 3.52 (s, 3H, OCH$_3$), 4.95 (m, 1H, =CH), 5.35 (m, 1H, CHOAc)
3b	15	88/0.001	1665 (C=C), 1715 (C=O)	1.9 (m, 6H, 3×CH$_2$), 3.52 (s, 3H, OCH$_3$), 4.9 (m, 1H, =CH), 5.6 (m, 1H, CHOAc), 7.45 (m, 3H$_{arom}$), 8.10 (m, 2H$_{arom}$)
3c	91	78/0.001	1665 (C=C), 1740 (C=O)	1.40–2.20 (m, 6H, 3×CH$_2$), 3.53 (s, 3H, OCH$_3$), 3.85 (s, 3H, CO$_2$CH$_3$), 4.80–4.95 (m, 1H, CHO), 5.05–5.20 (m, 1H, =CH)
3d	65	64/0.2	1670 (C=C), 1750 (C=O)	0.25 [s, 9H, Si(CH$_3$)$_3$], 1.40–2.10 (m, 6H, 3×CH$_2$), 4.78 (s, 3H, CO$_2$CH$_3$), 4.95–5.10 (m, 2H, 2×CH)

(b) Acyloxylation of Enol Ethers **1a, 13a–c**; *General Procedure:* A solution of **1a, 13a–c** (0.1 mol) in anhyd. CH$_2$Cl$_2$ was heated to gentle reflux. An equimolar amount of freshly prepared dimethyl peroxydicarbonate (**2c**; 15 g, 0.1 mol) in CH$_2$Cl$_2$ was added dropwise under stirring. Complete conversions needed further stirring: 30 min in the case of **1a**, 12 h in cases of **13a** and **13b**; in the case of **13c** the mixture must be stirred for 12 h under rather vigorous reflux. Compound **13a** (11.9 g, 0.122 mol) gave 12.27 g (55 %) of a 57:43 mixture of **14a** and **15a**, bp 55 °C/0.001 Torr; **1a** (16.8 g, 0.15 mol) afforded 22.2 g (91 %) of **3c**, bp 78 °C/0.001 Torr; **13b** (12.62 g, 0.1 mol) yielded 14.6 g (63 %) of **15b**, bp 78–90 °C/0.001 Torr. Diphenyl phosphinic acid (100 mg) catalyzed elimination of MeOH at 140 °C from **15b** (13.6 g, 0.06 mol) gave 7.81 g (65 %) of **14b**, bp 57–61 °C/0.001 Torr. Compound **13c** (14.03 g, 0.1 mol) yielded 18.3 g (81 %) of a 65:35 mixture of **14c** and **15c**, which was immediately treated in the same manner as before to give 16.47 g (77 %) pure **14c**, bp 71–75 °C/0.001 Torr.

Transformation Reactions of 3c:

(a) *Formation of 2-Methoxycyclohexa-1,3-diene* (**5**) *by Thermolysis:* Neat **3c** (10 g, 0.054 mol) was heated at 280 °C under N$_2$ in a distillation apparatus of trimethylsilylated glassware using a metal bath. The resulting distillate was added dropwise onto KOH pellets under ice cooling. After filtration the crude distillate was fractionated in vacuum yielding 5.1 g (86 %) of **5**; bp 26 °C/0.001 Torr.

(b) *Acidic Hydrolysis of* **3c** *to 2-(Methoxycarbonyloxy)cyclohexanone* (**6c**): A solution of **3c** (9.3 g, 0.05 mol) in CH$_2$Cl$_2$ (50 mL) was heated to reflux with conc. HCl (15 mL) and H$_2$O (15 mL) for 30 min. After cooling the organic layer was separated, washed with H$_2$O and aq NaHCO$_3$ solution and dried (MgSO$_4$). After evaporation of the solvent, the residual oil was triturated with EtOAc to give colorless crystals of **6c**; yield: 6.2 g (72 %); mp 65 °C (EtOAc).

(c) *Alkaline Hydrolysis of* **3c** *to 2-Methoxycyclohex-2-en-1-ol* (**7**): A mixture of **3c** (40 g, 0.215 mol) and a sat. solution of KOH in MeOH was stirred for 30 min at r.t. MeOH was evaporated and the residue extracted continuously with Et$_2$O for 10 h. Distillation of Et$_2$O in vacuum afforded 20.4 g (76 %) of **7** as a colorless liquid, bp 87–88 °C/13 Torr (Lit.[24] bp 92–98 °C/15 Torr).

The product **7** (1.3 g, 0.01 mol) was benzoylated with benzoyl chloride (1.4 g, 0.01 mol) in pyridine (3 mL) at r.t. for 18 h. After usual workup, bulb-to-bulb distillation afforded 1.85 g (79 %) of **3b** (Table 1). For an additional proof, the alcohol **7** (5.1 g, 0.04 mol) was hydrolysed with conc. HCl as described for **3c** (see above) to give dimeric 2-hydroxycyclohexanone (2.8 g, 62 %) as white powder; mp 112 °C.

(d) *Addition of DPDC* (**2c**) *to the C,C-Double Bond of 1-Methoxycyclohex-1-en-6-yl Methyl Carbonate* (**3c**); *2-Methoxy-1,2,3-tris(methoxycarbonyloxy)cyclohexane* (**8**): A solution of **2c** (0.125 mol) in CH$_2$Cl$_2$ (250 mL) was added dropwise under stirring to a solution of **3c** (23.3 g, 0.125 mol) in CH$_2$Cl$_2$ (20 mL) maintained under gentle reflux at 50 °C (bath). Stirring was continued for 36 h and traces of unconsumed peroxide were destroyed by addition of a catalytic amount of CuCl (3 g). The reaction mixture was filtered and CH$_2$Cl$_2$ removed in a rotary evaporator. The oily residue was dissolved in

Table 2. Spectral Data of Enol Ethers **14a–c** and Their Corresponding Acetals **15a–c**

Product	IR (neat) ν (cm^{-1})	^{1}H NMR (CDCl$_3$/TMS) δ, J (Hz)	^{13}C NMR (CDCl$_3$/TMS) δ, J (Hz)
14a	1655 (C=C), 1750 (C=O)	1.70–2.51 (m, 4H, CH$_2$CH$_2$), 3.64 (s, 3H, OCH$_3$), 3.78 (s, 3H, CO$_2$CH$_3$), 4.82 (m, 1H, CHO), 5.44 ((m, 1H, =CH)	29.5, 30.6 (CH$_2$), 54.6 (OCH$_3$), 57.1 (CO$_2$CH$_3$), 80.9 (CHO), 109.7 (=CH), 155.3 (C=CO), 156.9 (C=O)
14b	1665 (C=C), 1750 (C=O)	1.50–2.00 (m, 8H, 4×CH$_2$), 3.47 (s, 3H, OCH$_3$), 4.79 (s, 3H, CO$_2$CH$_3$), 4.90 (t, 1H, J = 6.3, CHO), 5.24 (m, 1H=CH)	23.3, 24.2, 26.4, 29.1 (CH$_2$), 54.4 (OCH$_3$), 78.1 (CHO), 100.4 (=CH), 155.1 (C=CO), 156.8 (C=O)
14c	1670 (C=C), 1755 (C=O)	1.31–1.80 (m, 10H, 5×CH$_2$), 3.53 (s, 3H, OCH$_3$), 3.77 (s, 3H, CO$_2$CH$_3$), 4.70 (t, 1H, J = 6.6, CHO), 5.52 (t, 1H, J = 4.5, =CH)	23.5, 24.3, 26.5, 31.5, 33.1 (CH$_2$), 54.4 (OCH$_3$), 54.5 (CO$_2$CH$_3$), 73.9 (CHO), 97.4 (=CH), 153.0 (C=CO), 155.1 (C=O)
15a	1750 (C=O)	1.70–2.51 (m, 6H, 3×CH$_2$), 3.25, 3.27 (2s, 6H, 2×OCH$_3$), 3.79 (s, 3H, CO$_2$CH$_3$), 4.91 (m, 1H, CHO)	19.1, 26.1, 29.2 (CH$_2$), 48.7, 50.7 (OCH$_3$), 54.6 (CO$_2$CH$_3$), 78.5 (CHO), 100.3 (C$_{quart}$), 155.7 (C=O)
15b	1750 (C=O)	1.47–1.74 (m, 6H, 3×CH$_2$), 1.75–1.84 (m, 4H, 2×CH$_2$), 3.18, 3.22 (2s, 6H, 2×OCH$_3$), 3.79 (s, 3H, CO$_2$CH$_3$), 5.46 (m, 1H, CHO)	20.2, 20.4, 25.9, 26.5, 30.8 (CH$_2$), 48.0 (OCH$_3$), 54.2 (CO$_2$CH$_3$), 76.4 (CHO), 102.4 (C$_{quart}$), 155.1 (C=O)
15c	1755 (C=O)	1.20–2.58 (m, 12H, 6×CH$_2$), 3.20, 3.22 (2s, 6H, 2×OCH$_3$), 3.77 (s, 3H, CO$_2$CH$_3$), 4.84 (t, 1H, J = 6.7, CHO)	

a few mL of Et_2O and stored for 2 d at − 20 °C. The formed crystals were isolated by suction, recrystallized from Et_2O and dried in a desiccator, colorless crystals of **8** were obtained; yield: 25.6 g (60 %), mp 131.7 °C.

For decarboxylation, **8** (1.5 g, 4.5 mmol) was dissolved in a mixture of CH_2Cl_2 (60 mL) and absolute MeOH (5 mL). The solution was refluxed for 4 d and the solvent removed as before. The oily residue crystallized after addition of Et_2O (ca. 1 mL); colorless crystals of 2,2-dimethoxy-1,3-bis(methoxycarbonyloxy)cyclohexane (**9**) were obtained; yield: 1.29 g (98 %); mp 131 °C (Et_2O).

2-Hydroxycyclohexa-1,3-dione (12):
A mixture of the acetal **9** (1.16 g, 4 mmol) and KOH (0.5 g, 9 mmol) in H_2O (30 mL) and MeOH (20 mL) was stirred for 24 h at 50 °C. The resulting yellow solution was extracted with $CHCl_3$, the organic phase dried ($MgSO_4$) and the solvent evaporated in vacuum in a rotary evaporator. The oily residue was crystallized from a few mL of anhydr. Et_2O, affording colorless crystals of 1,3-dihydroxy-2,2-dimethoxycyclohexane (**10**); yield: 0.65 g (92 %), mp 113.6 °C (Et_2O). A solution of **10** (0.25 g, 1.4 mmol) in absolute CH_2Cl_2 (10 mL) was added to a vigorously stirred suspension of pyridinium chlorochromate (0.4 g, 1.8 mmol) in absolute CH_2Cl_2 (30 mL) and the mixture was stirred for 16 h at r.t. Silica gel (5 g) was added and the mixture filtered and evaporated. Crude 2,2-dimethoxy-3-hydroxycyclohexanone (**11**) was obtained as a yellow oil; yield: 0.15 g (61 %), which was directly hydrolyzed to **12** by heating with 6 N HCl (10 mL) for 10 min at 80 °C. Formation of reductone **12**[13a] was proved by a positive coloration with methanolic $FeCl_3$ (blue color) as well as by discoloration of Tillmans' reagent.[13b] Addition of excess $Pb(OAc)_2 \cdot 3H_2O$ (0.5 g, 1.3 mmol) precipitated its lead chelate; yield: 0.2 g (75 %), insoluble in H_2O.

Table 3. Spectral Data of Compounds Obtained from Transformation Reactions of **3b** (Schemes 2 and 3)

Product	IR (neat/KBr) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)
5	1585, 1650 (C=C)	2.16 (m, 4H, $2 \times CH_3$), 3.62 (s, 3H, OCH_3), 4.75 (m, 1H, =CH), 6.00 (m, 2H, CH=CH)
6c	1715, 1745 (C=O)	2.05 (m, 8H, $4 \times CH_2$), 3.92 (s, 3H, CO_2CH_3), 5.14 (m, 1H, CHO)
8[a]	1755 (C=O)	1.42–1.54 (m, 1H, CH_2CHHCH_2), 1.79–1.95 (m, 5H, CH_2CHHCH_2), 3.57 (s, 3H, OCH_3), 3.78 (s, 3H, CO_2CH_3), 3.79 (s, 6H, $2 \times CO_2CH_3$), 5.45–5.48 (m, 2H, $2 \times$ CHO)
9[b]	1750 (C=O)	1.56–1.95 (m, 6H, $3 \times CH_2$), 3.24–3.28 (2s, 6H, $2 \times OCH_3$), 3.78 (s, 6H, $2 \times CO_2CH_3$), 4.95 (m, 2H, CHO)
10	3340 (OH)	1.07–2.11 (m, 6H, $3 \times CH_2$), 3.1 (d, 2H, J = 6.6, OH), 3.20, 3.38 (2s, 6H, $2 \times OCH_3$), 3.86–4.11 (m, 2H, $2 \times$ CH)
11	1750 (C=O), 3040 (OH)	1.60–2.90 (m, 6H, $3 \times CH_2$), 3.23 (s, 1H, OH), 3.36–3.51 (m, 6H, $2 \times OCH_3$), 4.20–4.36 (m, 1H, CH)

[a] ^{13}C NMR ($CDCl_3$/TMS): δ = 17.6, 27.4 ($2 \times CH_2$), 52.0 (OCH_3), 54.4, 54.8 ($2 \times CO_2CH_3$), 75.0 (CHO), 102.8 (C_{quart}), 152.0, 154.8 ($2 \times$ C=O).

[b] ^{13}C NMR ($CDCl_3$/TMS): δ = 14.9, 27.1 ($2 \times CH_2$), 48.7 (OCH_3), 54.7 (CO_2CH_3), 73.5 (CHO), 96.8 (C_{quart}), 155.2 (C=O).

6-Methoxycarbonyloxy-1-trimethylsiloxycyclohex-1-ene (3d):
A solution of **2c** in CH_2Cl_2 (0.2 mol) was added dropwise to a boiling mixture of enol silyl ether **1b**[20] (37.5 g, 0.22 mol) and absolute CH_2Cl_2 (100 mL). After continuous reflux for 14 h, peroxide **2c** was quantitatively consumed. Fractionated distillation afforded 31.8 g (65 %) of **3d**; bp 64 °C/0.2 Torr. For structural proof, a solution of **3d** (24.4 g, 0.1 mol) in CH_2Cl_2 (100 mL) was refluxed for 30 min with a mixture of conc. HCl (25 mL) and H_2O (25 mL). Usual workup yields 13.8 g (80 %) of **6c**; mp 65 °C (EtOAc).

1:1 Addition of 2c to Aldehyde Enol Ethers 16–18:
A solution of **2c** in CH_2Cl_2 (0.1 mol) was added dropwise to a stirred solution of *i*-butyl vinyl ether (**16**) (10.0 g, 0.1 mol) in absolute CH_2Cl_2 (50 mL), at 50 °C (bath).[25] Stirring at 50 °C was continued for 36 h, unreacted **2c** was decomposed by addition of a catalytic amount of CuCl (3 g). After filtration and distillation 1,2-bis(methoxycarbonyloxy)-1-(2-methylpropyloxy)ethane (**19**) was obtained as a colorless oil, yield: 19.5 g (78 %), bp 76 °C/0.001 Torr.

At 70 °C, 2,3-dihydrofuran (**17**; 6 g, 86 mmol) reacted with **2c** (12.9 g, 86 mmol) to give **20** (11.9 g, 63 %, 55:45 mixture of isomers) as a colorless, viscous oil, bp 92 °C/0.001 Torr. In a similar manner, the reaction of 2,3-dihydropyran (8.41 g, 0.1 mol) with **2c** (15 g, 0.1 mol) at 80 °C afforded **21** (10.1 g, 43 %, 50:50 mixture of isomers) as a pale-yellow viscous oil; bp 101 °C/0.001 Torr.

We are indebted to Thomas Heisel for graphical arrangement of the manuscript.

Table 4. Spectral Data of 1 : 1 Addition Products **19**–**21** of **2c** to Aldehyde Enol Ethers **16**–**18**

Product	IR (neat) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ
19	1768 (C=O)	0.90, 0.91 (d, 6H, $2 \times CH_3$), 1.81–1.93 (m, 1H, CH), 3.36–3.62 (m, 2H, CH_2O), 3.80, 3.81 (2s, 6H, $2 \times OCH_3$), 4.24 (dd, 2H, CH_2OC=O), 5.87 (t, 1H, J = 8.3, OCHOCO)	19.4 (CH_3), 28.3 (CH), 54.8 (OCH_3), 66.5 (OCH_2), 76.5 (CH_2OC=O), 97.9 (OCHOC=O), 154.8, 155.0 (C=O)
20	1750 (C=O)	2.10–2.22 (m, 2H, CH_2), 2.37–2.45 (m, 2H, CH_2), 3.798, 3.807, 3.813, 3.824 (4s, 12H, $4 \times OCH_3$), 3.98–4.04 (q, 1H, J = 7.6, HCHO), 4.16–4.23 (m, 3H, $3 \times$ HCHO), 5.06–5.11 (m, 1H, CH_{ax}–O), 5.13–5.15 (dd, 1H, CH_{ax}–O), 6.13 (s, 1H, OCH_{ax}–O), 6.21–6.22 (d, 1H, J = 4.1, OCH_{eq}–O)	26.7, 28.8 (CH_2), 54.6, 54.7, 54.9 (CH_3O), 66.1, 68.1 (CH_2O), 75.2, 80.0, 96.6, 102.3 (CHO), 154.2, 154.6, 154.8 (C=O)
21	1770 (C=O)	1.51–2.12 (m, 8H, $2 \times CH_2CH_2$), 3.7 (m, 2H, $2 \times OCHH_{ax}$), 3.78, 3.80, 3.81, 3.82 (4s, 12H, $4 \times OCH_3$), 3.92 (m, 2H, $2 \times OCHH_{eq}$), 4.64 (q, 1H, J = 4.7, CH_{ax}–O), 4.76 (m, 1H, CH_{eq}–O), 5.80 (d, 1H, $J_{a,e}$ = 2.9, OCH_{eq}–O), 6.06 (d, 1H, J_{ee} = 3.1, OCH_{eq}–O)	14.7, 18.2, 18.6 (CH_2), 49.2, 49.4 (OCH_3), 55.6, 57.0 (OCH_2), 65.4, 66.9 (OCH), 88.1, 88.9 (OCHO), 149.1, 149.5, 149.6 (C=O)

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