

# Acyloxylation of 1-methoxycyclohex-1-ene and other enol ethers with dimethyl peroxydicarbonate

Kurt Schank\*, Horst Beck, Susanne Pistorius, and Thomas Rapold

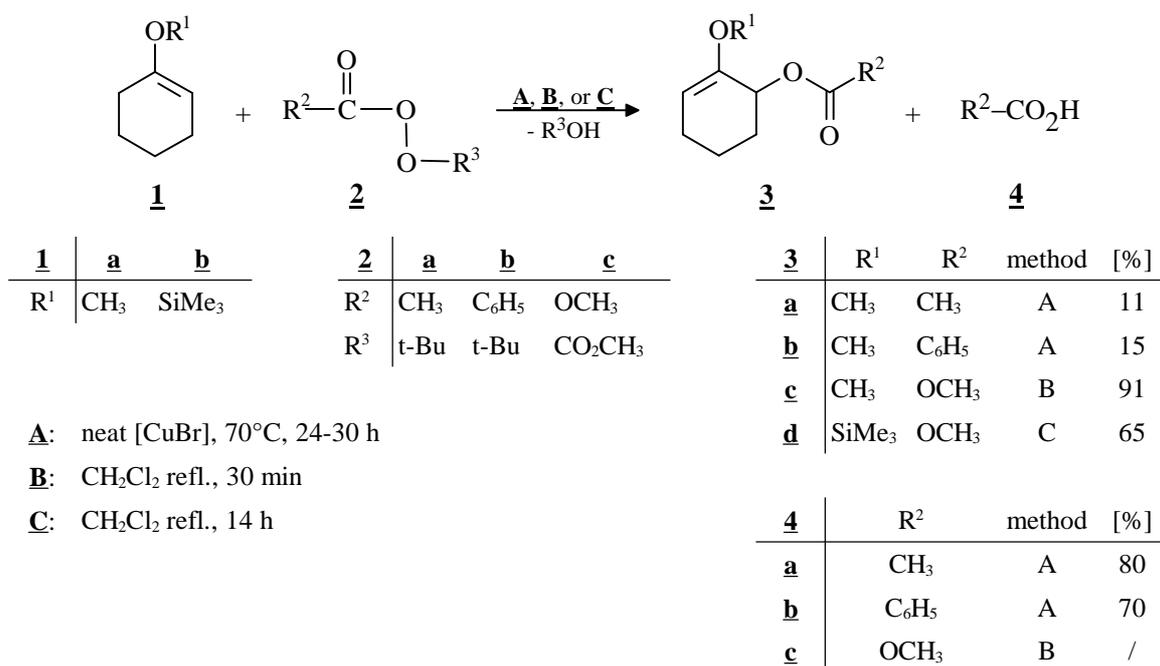
Fachrichtung 11.2 Organische Chemie der Universität des Saarlandes, D-66041 Saarbrücken, Germany

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 with 1-methoxycyclohex-1-ene (**1a**) are compared with copper(I)-salt catalyzed acyloxylation by means of tert. butyl peroxy-carboxylates **2a**, **b**.

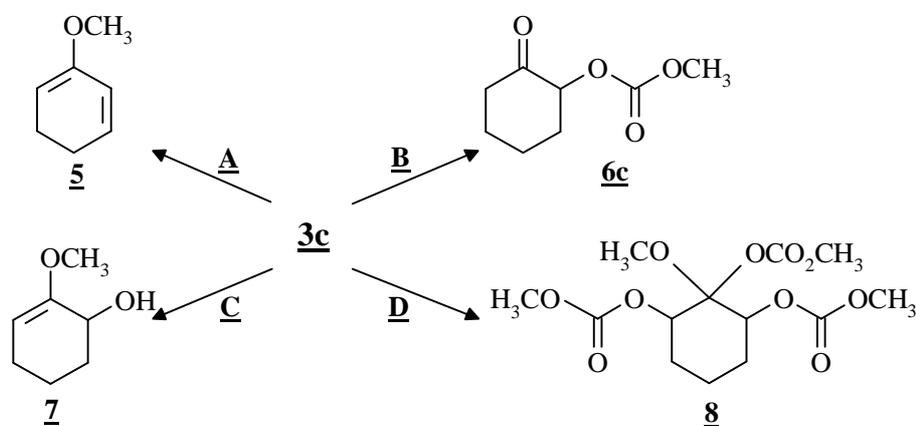
Allylic hydrogens in alkenes are easily replaced by bromine via a  $S_R$  reaction using N-bromosuccinimide (NBS)<sup>1)</sup>. Corresponding replacement of allylic hydrogen by acyloxy groups occurs with tert. butyl peroxy-carboxylates **2** in the presence of cuprous salts as electron-transfer-catalysts (ETC)<sup>2)</sup> during the Kharasch-Sosnovsky reaction<sup>3)</sup> Whereas 1-halogenocycloalk-1-enes react with NBS via  $S_R$  yielding 1,3-disubstitution products<sup>4)</sup>, the related 1-alkoxycycloalk-1-enes show 1,2-disubstitution (or addition) products<sup>5)</sup>. In order to investigate whether the latter compounds would form 1,2- or 1,3-substitution products, 1-methoxycyclohex-1-ene (**1a**) was acyloxyated by tert. butyl peracetate (**2a**) or by 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 main products<sup>6)</sup>. The low yields of desired **3a**, **b** could not be enhanced in the presence of bases (potassium tert. butylate or calcium hydride). Therefore, DPDC<sup>7)</sup> was utilized as acyloxyating agent because elimination of methyl monocarbonate (**4c**) instead of a carboxylic acid would lead to carbon dioxide and methanol. Additionally, higher reactivity of **2c** compared with **2a**, **b** (as a consequence of a particularly low O,O bond dissociation energy (BDE)<sup>8)</sup>) should not need copper(I)-catalysis<sup>9)</sup>, enol ethers as electron rich olefins reacted spontaneously with **2c**<sup>10)</sup>.

**Scheme 1:**



Since enol silyl ethers have been successfully acyloxylated by means of lead(IV)-carboxylates<sup>11)</sup> the reactivity of **1b** toward **2c** compared with **1a** was checked. The reaction rate showed to be markedly slower<sup>12)</sup>. **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 methoxycyclohexadiene **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**.

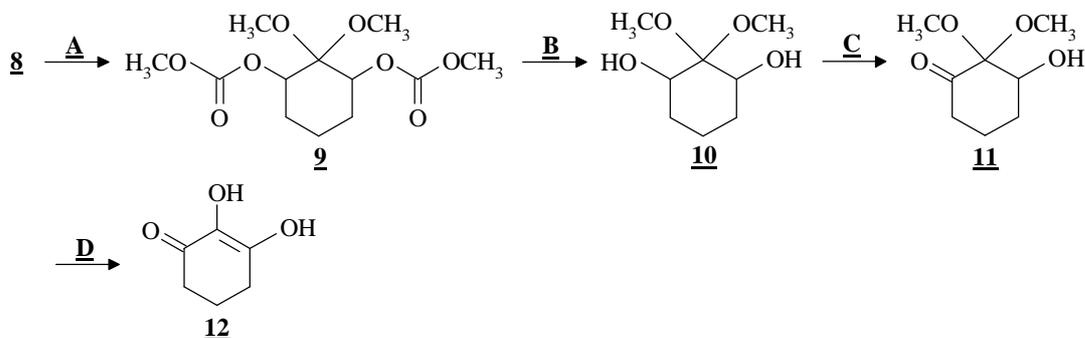
**Scheme 2:**



**A:** 280°C, 86%; **B:** H<sub>3</sub>O<sup>+</sup>, 72%; **C:** KOH/CH<sub>3</sub>OH, 76%; **D:** **3c**, CH<sub>2</sub>Cl<sub>2</sub> refl., 60%

For structural proof **7** was hydrolyzed by dilute mineral acid yielding the dimer of 2-hydroxycyclohexanone or was derivatized by means of benzoyl chloride/pyridine mixture yielding **3b**; furthermore, **8** has been utilized as primary product of a new synthesis for dihydro pyrogallol **12**.

**Scheme 3:**

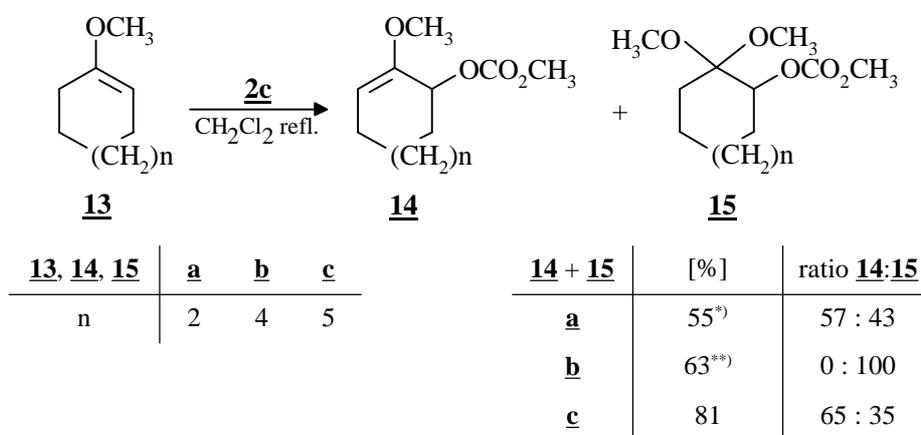


**A:** CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH, 98%; **B:** KOH/H<sub>2</sub>O, CH<sub>3</sub>OH, 50°C, 92%; **C:** PCC, CH<sub>2</sub>Cl<sub>2</sub>, 61%; **D:** H<sub>3</sub>O<sup>+</sup>, 80°C, 75%

**12** has not been isolated directly, the characteristic reducing properties have been confirmed qualitatively via positive ferric chloride and Tillmans tests<sup>13</sup>, for quantitative determination highly water soluble **12** was precipitated by lead(II)-acetate as its insoluble lead(II)-complex<sup>13</sup>.

In order to gain more insight into enol ether - DPDC reactions further enol ethers have been subjected to this acyloxylation procedure. Ketone enol ethers **13a**, **b**, **c** (homologous to **1a**) did not lead to exclusive formation of acyloxyated 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 acyloxyated cycloalkanone dimethyl acetals **15a**, **b**, **c**.

**Scheme 4:**

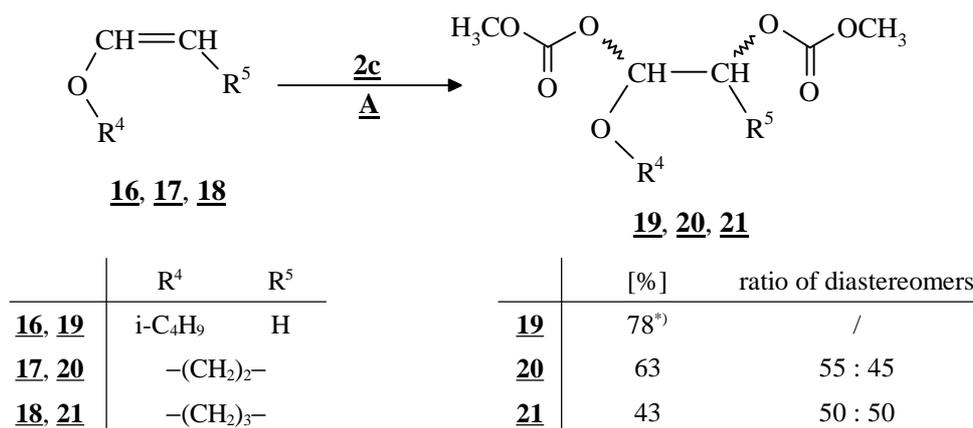


<sup>\*)</sup> large amounts of polymeric by-products

<sup>\*\*)</sup> 3% bis-acyloxylation product in analogy to **8** during 1:1 conversion

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 acyloxylation of **14a-c** were possible, however, these conversions led to crude mixtures of stereomers and other products. Vinyl and vinyleno ethers **16**, **17**, **18** (i.e. enol ethers from aldehydes) suffered exclusive addition of **2c** to their double bonds yielding **19**, **20**, **21**. **20**, **21** appeared as mixtures of diastereomers.

**Scheme 5:**

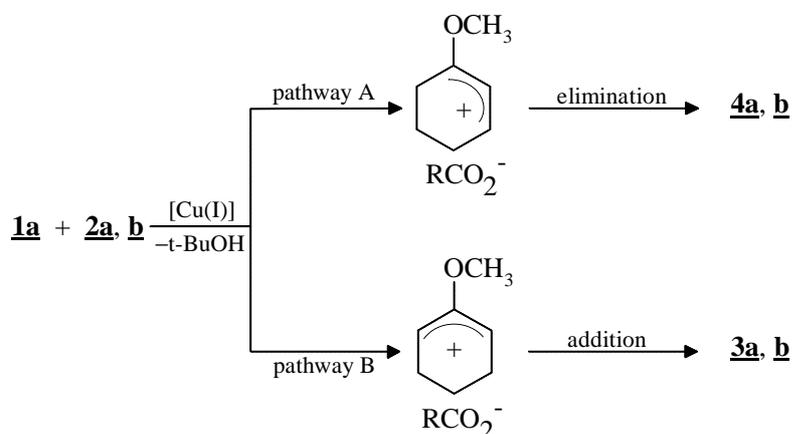


**A**: CH<sub>2</sub>Cl<sub>2</sub>, bath of 50°C, 36 h; <sup>\*)</sup> a bath of 70-80°C gave rise to 57% methoxycarbonyl-oxyacetaldehyde i-butyl methyl acetal instead of **19**

**Mechanistic Proposal.**

It is suggested that formation of carboxylic acids **4** as elimination products on the one hand and formation of desired enol ethers **3** as substitution products of acyloxylation of **1a** by **2a**, **b** under Kharasch-Sosnovsky conditions on the other hand are due to the intermediacy of two different isomeric methoxy allylic cations.

**Scheme 6:**



Pathway A would accord to the Kharasch-Sosnovsky mechanism<sup>3,14)</sup> 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<sup>15)</sup>) 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 SET<sup>16)</sup> 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<sup>17)</sup>.

Melting points are determined by means of a Fus-O-mat (Heraeus) or a copper block, IR spectra are recorded on a Beckman IR-33 (films or KBr-pellets), NMR spectra are recorded on Varian EM360, Bruker WP80 or AM400 spectrometers (solutions in CDCl<sub>3</sub> with TMS as internal standard), elemental analyses are obtained from a Carlo Erba analyzer. TLC control of reaction mixtures are carried out using foils Alugram<sup>®</sup> SIL G/UV<sub>254</sub> from Macherey and Nagel. The following compounds are prepared according to known procedures: 1-Methoxy-1-cycloalkenes **1a, 13a-c**<sup>18)</sup>, in particular **1a**<sup>19)</sup>, 1-trimethylsiloxy-1-cyclohexene (**1b**)<sup>20)</sup>, dimethyl peroxy-dicarbonate (**2c**)<sup>21)</sup>. Other reagents used are commercially available. t-Butyl peroxyesters **2a, b** are dried prior to use according to a known procedure<sup>22)</sup>.

Caution: All handling with peroxy compounds is carried out behind a safety shield in a hood. Concentration of reaction mixtures presupposes decomposition of unreacted peroxide by boiling with cuprous chloride. No explosions are observed following this procedure.

Acyloxylation of **1a** with **2** under Kharasch-Sosnovsky conditions: 1-Methoxy-1-cyclohexene (**1a**) (56g, 0.5 mol resp. 136g, 1.2 mol) and a catalytic amount of cuprous bromide (0.5 g resp. 2g) are stirred and heated to 70°C under nitrogen atmosphere. tert.-Butyl peracetate (**2a**) (30g, 0.22 mol) resp. tert.-butyl perbenzoate (**2b**) (97g, 0.5 mol) are added dropwise, and stirring is continued at 70°C until the deep blue color disappears (ca. 44h resp. 30h). The cooled reaction mixture is diluted with twice of its volume of ether, copper salts are removed by filtration, and acetic resp. benzoic acid are extracted with aqueous potassium carbonate and determined acidimetrically; yields 80% resp. 70%. The organic layer is dried with MgSO<sub>4</sub> and separated under usual distillation conditions:

**Table 1:** Data of **3a** and **3b**

	Yield [%]	b.p. <sub>0.001</sub> [°C]	IR [cm <sup>-1</sup> ]		<sup>1</sup> H-NMR [δ ppm, TMS internal] (Varian EM360)
<b>3a</b>	11	62	C=C 1625	C=O 1740	1.9 (m, 6H, 3CH <sub>2</sub> ); 2.1 (s, 3H, CH <sub>3</sub> CO); 3.52 (s, 3H, OCH <sub>3</sub> ); 4.95 (m, 1H, CH-vinyl); 5.35 (m, 1H, <u>CH</u> OCOCH <sub>3</sub> ).
<b>3b</b>	15	88	1665	1715	1.9 (m, 6H, 3CH <sub>2</sub> ); 3.52 (s, 3H, OCH <sub>3</sub> ); 4.9 (m, 1H, CH-vinyl); 5.6 (m, 1H, <u>CH</u> OCOC <sub>6</sub> H <sub>5</sub> ); 7.45, 8.1 (2m, 3+2H, CH <sub>ar</sub> )

Hydrolysis of **3b** by refluxing a CH<sub>2</sub>Cl<sub>2</sub> solution with 6N aqueous hydrochloric acid for 2h afforded 2-benzoyloxycyclohexanone, m.p. 84°C (m.p. 82-84°C<sup>23</sup>), 82% yield.

Mono- and bis-acyloxylation of 1a with DPDC (2c) and subsequent conversions of the resulting reaction products. a) Preparation of a solution of **2c**<sup>24</sup>: Water (200 mL) is added to a mixture of methyl chloroformate (37.8 g, 0.4 mol) and CH<sub>2</sub>Cl<sub>2</sub> (300 mL) in a 2L beaker. After cooling to 5°C (ice bath) sodium peroxide (17.2g, 0.22 mol) is added in small portions under vigorous mechanical stirring, while the temperature does not exceed 10°C. Stirring is continued for 2h under further cooling, finally the two liquid phases are separated. The organic phase is washed with ice water and dried over K<sub>2</sub>CO<sub>3</sub> at 0°C for 2h. Iodometric titration of an aliquot part indicates a yield of ca. 66% (20g, 0.14 mol) **6**. b) General acyloxylation procedure: 1-Methoxy-1-cycloalkenes **1a**, **13a-c** (0.1 mol) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) are heated to gentle reflux. Equimolar amounts of freshly prepared peroxydicarbonate **2c** in CH<sub>2</sub>Cl<sub>2</sub> are added dropwise under stirring. Complete conversions need further stirring under these conditions, 30 min in the case of **1a**, 12h in cases of **13a** and **13b**; in the case of **13c** the mixture must be stirred for 12 h under rather vigorous reflux. **13a** (11.9g, 0.122 mol) yields 12.27g (55%) of a 57:43-mixture of **14a** and **15a**, b.p. 55°C/10<sup>-3</sup> Torr; **1a** (16.8g, 0.15 mol) yields 22.2g (91%) of **3c**, b.p. 78°C/10<sup>-3</sup> Torr; **13b** (12.62g, 0.1 mol) yields 14.6g (63%) of **15b**, b.p. 78-90°C/10<sup>-3</sup> Torr; diphenyl phosphinic acid (100 mg) catalyzed elimination of methanol at 140°C from **15b** (13.6g, 0.06 mol) yields 7.81g (65%) of **14b**, b.p. 57-61°C/10<sup>-3</sup> Torr. **13c** (14.03g, 0.1 mol) yields 18.3g (81%) of a 65:35 mixture of **14c** and **15c**, which is immediately treated in the same manner as before to give 16.47g (77%) pure **14c**, b.p. 71-75°C/10<sup>-3</sup> Torr.

**Table 2:** Spectral data of enol ethers **14a**, **3a**, **14b**, **14c** and corresponding acetals **15**

Product	IR, $\nu$ ( $\text{cm}^{-1}$ )		$^1\text{H}$ NMR, $\delta$	$^{13}\text{C}$ NMR, $\delta$
<b>14a</b>	C=C 1655	C=O 1750	1.70-2.51 (m, 4H, $\text{CH}_2\text{-CH}_2$ ); 3.64 (s, 3H, $\text{OCH}_3$ ); 3.78 (s, 3H, $\text{CO}_2\text{CH}_3$ ); 4.82 (m, 1H, $\text{CH-O}$ ); 5.44 (m, 1H, $\text{CH=C}$ )	29.5, 30.6 ( $\text{CH}_2$ ); 54.6 ( $\text{OCH}_3$ ); 57.1 ( $\text{CO}_2\text{CH}_3$ ); 80.9 ( $\text{CH-O}$ ); 109.7 ( $\text{CH=C}$ ); 155.3 ( $\text{C=C-O}$ ); 156.9 ( $\text{C=O}$ )
<b>15a</b>		1.750	1.70-2.51 (m, 6H, $3\text{CH}_2$ ); 3.25, 3.27 (2s, 6 H, 2 $\text{OCH}_3$ ); 3.79 (s, 3H, $\text{CO}_2\text{CH}_3$ ); 4.91 (m, 1H, $\text{CH-O}$ )	19.1, 26.1, 29.2 ( $\text{CH}_2$ ); 48.7, 50.7 ( $\text{OCH}_3$ ); 54.6 ( $\text{CO}_2\text{CH}_3$ ); 78.5 ( $\text{CH-O}$ ); 100.3 ( $\text{C}_{\text{quart.}}$ ); 155.7 ( $\text{C=O}$ )
<b>3c<sup>a)</sup></b>	1665	1740	1.40-2.20 (m, 6H, $3\text{CH}_2$ ); 3.53 (s, 3H, $\text{OCH}_3$ ); 3.85 (s, 3H, $\text{CO}_2\text{CH}_3$ ); 4.8-4.95 (m, 1H, $\text{CH-O}$ ); 5.05-5.20 (m, 1H, $\text{CH=C}$ )	
<b>14b</b>	1665	1750	1.50-2.0 (m, 8H, $4\text{CH}_2$ ); 3.47 (s, 3H, $\text{OCH}_3$ ); 4.79 (s, 3H, $\text{CO}_2\text{CH}_3$ ); 4.90 (t, 1H, $\text{CH-O}$ ); 5.24 (m, 1H, $\text{CH=C}$ )	23.3, 24.2, 26.4, 29.1 ( $\text{CH}_2$ ); 54.4 ( $\text{OCH}_3$ ); 78.1 ( $\text{CH-O}$ ); 100.4 ( $\text{CH=C}$ ); 155.1 ( $\text{C=C-O}$ ); 156.8 ( $\text{C=O}$ )
<b>15b</b>		1750	1.47-1.74 (m, 6H, $3\text{CH}_2$ ); 1.75-1.84 (m, 4H, $2\text{CH}_2$ ); 3.18, 3.22 (2s, 6H, $2\text{OCH}_3$ ); 3.79 (s, 3H, $\text{CO}_2\text{CH}_3$ ); 5.46 (m, 1H, $\text{CH-O}$ )	20.2, 20.4, 25.9, 26.5, 30.8 ( $\text{CH}_2$ ); 48.0 ( $\text{OCH}_3$ ); 54.2 ( $\text{CO}_2\text{CH}_3$ ); 76.4 ( $\text{CH-O}$ ); 102.4 ( $\text{C}_{\text{quart.}}$ ); 155.1 ( $\text{C=O}$ )
<b>14c</b>	1670	1755	1.31-1.80 (m, 10H, $5\text{CH}_2$ ); 3.53 (s, 3H, $\text{OCH}_3$ ); 3.77 (s, 3H, $\text{CO}_2\text{CH}_3$ ); 4.70 (t, 1H, $\text{CH-O}$ ); 5.52 (t, 1H, $\text{CH=C}$ )	23.5, 24.3, 26.5, 31.5, 33.1 ( $\text{CH}_2$ ); 54.4 ( $\text{OCH}_3$ ); 54.5 ( $\text{CO}_2\text{CH}_3$ ); 73.9 ( $\text{CH-O}$ ); 97.4 ( $\text{CH=C}$ ); 153.0 ( $\text{C=C-O}$ ); 155.1 ( $\text{C=O}$ )
<b>15c</b>		1.755	1.20-2.58 (m, 12H, $6\text{CH}_2$ ); 3.20, 3.22 (2s, 6H, $2\text{OCH}_3$ ); 3.77 (s, 3H, $\text{CO}_2\text{CH}_3$ ); 4.84 (t, 1H, $\text{CH-O}$ )	

a)  $\text{C}_9\text{H}_{14}\text{O}_4$  (186.2) calc. C 58.05 H 7.58 found C 57.91 H 7.59

**Conversions of 3c.** a) Formation of 2-methoxy-1,3-cyclohexadiene (**5**) by thermolysis: Neat **3c** (10g, 0.054 mol) is heated under nitrogen in a distillation apparatus of trimethylsilylated glass ware using a metal bath of  $280^\circ\text{C}$ . The resulting distillate is dropped onto potassium hydroxide pellets under ice cooling. After filtration the crude distillate is fractionated i. vac. yielding 5.1g (86%) **5**, b.p.  $26^\circ\text{C}/10^{-3}$  Torr. b) Acid hydrolysis of **3c** yielding 2-methoxycarbonyloxy-cyclohexanone (**6c**): **3c** (9.3g, 0.05 mol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) is heated to reflux with conc. hydrochloric acid (15 mL) and water (15 mL) for 30 min. After cooling the organic layer is separated, washed with water and aqueous  $\text{NaHCO}_3$  solution and dried with  $\text{MgSO}_4$ . After evaporation of the solvent, the residual oil is scratched with a glass bar after addition of a few drops of ethyl acetate yielding colorless crystals of **6c**, 6.2g (72%), m.p.  $65^\circ\text{C}$  (ethyl acetate). c) Alkaline hydrolysis of **3c** yielding 2-methoxy-2-cyclohexen-1-ol (**7**): **3c** (40g, 0.215 mol) and a saturated solution of KOH in methanol are stirred for 30 min at R.T. Methanol is evaporated and the residue is extracted continuously with ether for 10 h. Distillation of the ether extract, finally i. vac., afforded 20.4g (76%) **7** as colorless liquid, b.p.  $87\text{-}88^\circ\text{C}/13$  Torr

(92-98°C/15 Torr<sup>24</sup>). **7** (1.3g, 0.01 mol) in pyridine (3 mL) is benzoylated with benzoylchloride (1.4g, 0.01 mol) at R.T. for 18 h. After usual work-up, microdistillation affords 1.85g (79%) **3b** (cf. aforementioned data). For an additional proof **7** (5.1g, 0.04 mol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) is hydrolyzed according to the procedure with **3c**. Dimeric 2-hydroxycyclohexanone (2.8g, 62%) is obtained as white powder, m.p. 112°C. d) Addition of **2c** to the C,C double bond of **3c** affording 2-methoxy-1,2,3-tris(methoxycarbonyloxy)-cyclohexane (**8**): A solution of **2c** (0.125 mol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) is added dropwise under stirring to a mixture of **2c** (23.3g, 0.125 mol) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) maintained under gentle reflux in a bath of 50°C. Stirring is continued for 36h and traces of non-consumed peroxide are destroyed by addition of a catalytical amount of cuprous chloride (3g). The reaction mixture is filtered and CH<sub>2</sub>Cl<sub>2</sub> is removed in a rotary evaporator. The oily residue is dissolved in a few mL of ether and stored for 2d at -20°C. The formed crystals are isolated by suction, recrystallized from ether and dried in a desiccator; colorless crystals of **8** are obtained, 25.6g (60%), m.p. 131.7°C. For decarboxylation, **8** (1.5g, 4.5 mmol) is dissolved in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (60 mL) and absolute methanol (5 mL). The solution is refluxed for 4d and the solvent is removed as before. The oily residue crystallized after addition of ether (ca. 1 mL); colorless crystals of 2,2-dimethoxy-1,3-bis-(methoxycarbonyloxy) cyclohexane (**9**) are obtained, 1.29g (98%), m.p. 131°C (ether).

Conversion of acetal **9** to reductone **12**<sup>13</sup> resp. its lead(II) salt: **9** (1.16g, 4 mmol) is stirred with a solution of KOH (0.5g, 9 mmol) in water (30 mL) and methanol (20 mL) for 24h at 50°C. The resulting yellow solution is extracted with CHCl<sub>3</sub>, the organic phase is dried with MgSO<sub>4</sub> and the solvent is evaporated i. vac. in a rotary evaporator; the oily residue is crystallized from a few mL of dry ether, affording colorless crystals of 1,3-dihydroxy-2,2-dimethoxycyclohexane (**10**), 0.65g (92%), m.p. 113.6°C (ether). **10** (0.25g, 1.4 mmol) in absolute CH<sub>2</sub>Cl<sub>2</sub> (10 mL) is added to a vigorously stirred suspension of pyridinium chlorochromate (0.4g, 1.8 mmol) in absolute CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and the mixture is stirred for 16h at R.T. Silica gel (5g) is added and the mixture is filtered and evaporated. Crude 2,2-dimethoxy-3-hydroxycyclohexanone (**11**) is obtained as a yellow oil, 0.15g (61%), which is directly hydrolyzed to **12** by heating with 6N hydrochloric acid (10 mL) for 10 min to 80°C; formation of reductone **12**<sup>13a</sup>) is proved by a positive coloration with methanolic ferric chloride (blue color) as well as by discoloration of Tillmans' reagent<sup>13b</sup>). Addition of excess lead(II)

acetate trihydrate (0.5g, 1.3 mmol) precipitates its lead chelate, 0.2g (75%), insoluble in water.

**Table 3:** Spectral data of compounds obtained from conversions of **3c** (cf. Scheme 3) and **1b**

Product	IR, $\nu$ (cm <sup>-1</sup> )			<sup>1</sup> H NMR, $\delta$	<sup>13</sup> C NMR, $\delta$
	C=C	C=O	OH		
<b>5</b>	1585 1650			2.16 (m, 4H, 2CH <sub>2</sub> ); 3.62 (s, 3H, OCH <sub>3</sub> ); 4.75 (m, 1H, =CH-); 6.00 (m, 2H, -CH=CH-)	
<b>6c</b>		1715 1745		2.05 (m, 8H, 4CH <sub>2</sub> ); 3.92 (s, 3H, CO <sub>2</sub> CH <sub>3</sub> ); 5.14 (m, 1H, CH-O)	
<b>8</b>		1755		1.42-1.54 (m, 1H, CH of CH <sub>2</sub> ); 1.79-1.95 (m, 5H, 2CH <sub>2</sub> + CH of CH <sub>2</sub> ); 3.57 (s, 3H, OCH <sub>3</sub> ); 3.78 (s, 3H, CO <sub>2</sub> CH <sub>3</sub> ); 3.79 (s, 6H, 2CO <sub>2</sub> CH <sub>3</sub> ); 5.45-5.48 (m, 2H, 2CH-O)	17.6, 27.4 (2CH <sub>2</sub> ); 52.0 (OCH <sub>3</sub> ); 54.4, 54.8 (2CO <sub>2</sub> CH <sub>3</sub> ); 75.0 (CH-O); 102.8 (C <sub>quart.</sub> ); 152.0, 154.8 (2C=O)
<b>9</b>		1750		1.56-1.95 (m, 6H, 3CH <sub>2</sub> ); 3.24-3.28 (2s, 6H, 2OCH <sub>3</sub> ); 3.78 (s, 6H, 2CO <sub>2</sub> CH <sub>3</sub> ); 4.95 (m, 2H, CH-O)	14.9, 27.1 (2CH <sub>2</sub> ); 48.7 (OCH <sub>3</sub> ); 54.7 (CO <sub>2</sub> CH <sub>3</sub> ); 73.5 (CH-O); 96.8 (C <sub>quart.</sub> ); 155.2 (C=O)
<b>10</b>			3340	1.07-2.11 (m, 6H, 3CH <sub>2</sub> ); 3.1 (d, J=6.6 Hz, 2H, OH); 3.20, 3.38 (2s, 6H, 2OCH <sub>3</sub> ); 3.86- 4.11 (m, 2H, 2CH)	
<b>11</b>		1750	3040	1.6-2.9 (m, 6H, 3CH <sub>2</sub> ); 3.23 (s, 1H, OH); 3.36- 3.51 (m, 6H, 2OCH <sub>3</sub> ); 4.20-4.36 (m, 1H, CH)	
<b>3d</b>	1670	1750		0.25 (s, 9H, SiMe <sub>3</sub> ); 1.4-2.1 (m, 6H, 3CH <sub>2</sub> ); 4.78 (s, 3H, CO <sub>2</sub> CH <sub>3</sub> ); 4.95-5.1 (m, 2H, 2CH)	

**6-Methoxycarbonyloxy-1-trimethylsiloxy-1-cyclohexene (3d):** A solution of **2c** in CH<sub>2</sub>Cl<sub>2</sub> (0.2 mol) is dropped to a boiling mixture of enol silylether **1b**<sup>20)</sup> (37.5g, 0.22 mol) and absolute CH<sub>2</sub>Cl<sub>2</sub> (100 mL). After continuous reflux for 14h peroxide **2c** is quantitatively consumed. Fractionated distillation yields 31.8g (65%) **3d**, b.p. 64°C/0.2 Torr. For structural proof, **3d** (24.4g, 0.1 mol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) is refluxed for 30 min with a mixture of conc. hydrochloric acid (25 mL) and water (25 mL). Usual work-up yields 13.8g (80%) **6c**, m.p. 65°C (ethyl acetate).

**1:1-additions of 2c to aldehyde enol ethers 16-18.** a) A solution of **2c** in CH<sub>2</sub>Cl<sub>2</sub> (0.1 mol) is dropped to a solution of i-butyl vinyl ether (**16**) (10.0g, 0.1 mol) in absolute CH<sub>2</sub>Cl<sub>2</sub> (50 mL), stirred in a bath of 50°C<sup>25)</sup>. Stirring at 50°C is continued for 36h, nonconverted **2c** is decomposed by addition of a catalytic amount of cuprous chloride (3g). After filtration and distillation 1,2-bis(methoxycarbonyloxy)-1-i-butoxy-ethane (**19**) is obtained as a colorless oil, 19.5g (78%), b.p. 76°C/10<sup>-3</sup> Torr. b) As before, but in a bath of 70°C, 2,3-dihydrofuran **17** (6g, 86 mmol) reacts with equimolar amount of **2c** yielding **20** (11.9 g (63%, 55:45 mixture of

isomers)) as a colorless, viscous oil, b.p. 92°C/10<sup>-3</sup> Torr. c) Correspondingly, but in a bath of 80°C, 2,3-dihydropyran (8.41g, 0.1 mol) reacts with equimolar amount of **2c** yielding **21** (10.1 g (43%,50:50 mixture of isomers)) as a pale-yellow viscous oil, b.p. 101°C/10<sup>-3</sup> Torr.

**Table 4:** 1:1 addition products **19-21** of **2c** to aldehyde enol ethers **16-18**

Product	IR, $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H NMR, $\delta$	<sup>13</sup> C NMR, $\delta$
<b>19</b>	C=O 1768	0.9, 0.91 (d, 6H, 2CH <sub>3</sub> ); 1.81-1.93 (m, 1H, CH); 3.36-3.62 (m, 2H, CH <sub>2</sub> -O); 3.80, 3.81 (2s, 6H, 2OCH <sub>3</sub> ); 4.24 (dd, 2H, CH <sub>2</sub> -O-C=O); 5.87 (t, 1H, O-CH-O-C=O)	19.4 (CH <sub>3</sub> ); 28.3 (CH); 54.8 (OCH <sub>3</sub> ); 66.5 (OCH <sub>2</sub> ); 76.5 (CH <sub>2</sub> -O-C=O); 97.9 (O-CH-O-C=O); 154.8, 155.0 (C=O)
<b>20</b>	1750	2.10-2.22 (m, 2H, CH <sub>2</sub> ); 2.37-2.45 (m, 2H, CH <sub>2</sub> ); 3.798, 3.807, 3.813, 3.824 (4s, 12H, 4OCH <sub>3</sub> ); 3.98-4.04 (q, 1H, H-CH-O); 4.16-4.23 (m, 3H, 3H-CH-O); 5.06- 5.11 (m, 1H, CH <sub>ax</sub> -O); 5.13-5.15 (dd, 1H, CH <sub>ax</sub> -O); 6.13 (s, 1H, O-CH <sub>ax</sub> -O); 6.21-6.22 (d, J=4.1 Hz, 1H, OCH <sub>eq</sub> -O)	26.7, 28.8 (CH <sub>2</sub> ); 54.6, 54.7, 54.9 (CH <sub>3</sub> O); 66.1, 68.1 (CH <sub>2</sub> -O); 75.2, 80.0, 96.6, 102.3 (CH-O); 154.2, 154.6, 154.8 (C=O)
<b>21</b>	1770	1.51-2.12 (m, 8H, 2CH <sub>2</sub> -CH <sub>2</sub> ); 3.7 (m, 2H, 2OCH-H <sub>ax</sub> ); 3.78, 3.80, 3.81, 3.82 (4s, 12H, 4OCH <sub>3</sub> ); 3.92 (m, 2H, 2OCH-H <sub>eq</sub> ); 4.64 (q, 1H, CH <sub>ax</sub> -O); 4.76 (m, 1H, CH <sub>eq</sub> -O); 5.80 (d, J <sub>ae</sub> = 2.9 Hz, O-CH <sub>eq</sub> -O); 6.06 (d, J <sub>ee</sub> = 3.1 Hz, 1H, O-CH <sub>eq</sub> -O)	14.7, 18.2, 18.6 (CH <sub>2</sub> ); 49.2, 49.4 (OCH <sub>3</sub> ); 55.6, 57.0 (OCH <sub>2</sub> ); 65.4, 66.9 (OCH); 88.1, 88.9 (O-CH-O); 149.1, 149.5 149.6 (C=O)

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