Protolysis of Cyclopropanes with Geminal Electronegative Substituents

Per Kolsaker and Ann Kristin Jensen

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo 3, Norway

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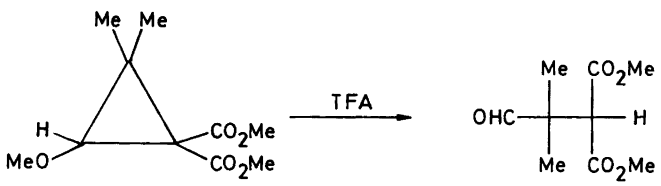
Cyclopropanes with geminal ester substituents decompose in anhydrous $HClO_4$/benzene solutions to give substituted γ-lactones; e.g. dimethyl 3,3-dimethyl-2-phenylcyclopropane-1,1-dicarboxylate (**1e**) is stereospecifically transformed to *trans*-γ,γ-dimethyl-α-methoxycarbonyl-β-phenyl-γ-butyrolactone (**8e**) in 87% yield. In TFA, **1e** is transformed to a mixture of two alkenes, viz. dimethyl (2-methyl-2-phenylpropylidene) malonate (**6e** – 58%) and dimethyl (2-methyl-1-phenylpropylidene) malonate (**5e** – 27%). Using TFA-*d*, no deuterium is found in **6e** and **5e**. When a methoxy substituent is present, aldehydo esters are formed; e.g. dimethyl 3,3-dimethyl-2-methoxycyclopropane-1,1-dicarboxylate (**1c**) is transformed in 92% yield to dimethyl (1-formyl-1-methylethyl) malonate (**11**). Four other dimethyl cyclopropane-1,1-dicarboxylates are decomposed. Geminal dinitriles do not decompose under the experimental conditions used, and geminal cyano esters react very sluggishly. Arguments are presented for protonation of the electronegative substituents being the first step in the decompositions. Upon prolonged standing the aldehydo diester **11** forms γ-methoxy-α-methoxycarbonyl-β,β-dimethyl-γ-butyrolactone (**12**). Deuteriation experiments using mass spectrometry indicate that, concerted with the ring formation, a complete scrambling of the methoxy groups takes place.

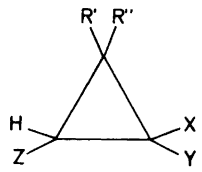
Some years ago we reported on the formation of substituted cyclopropanes in the reaction of nucleophiles with allylic bromides having electronegative γ-substituents.[1] In this connection we found that dimethyl 2-methoxy-3,3-dimethylcyclopropane-1,1-dicarboxylate (**1c**) very easily underwent 1,2-bond cleavage in trifluoroacetic acid (TFA) (Scheme 1).

Unsymmetrically substituted cyclopropanes are cleaved by acids of the type HA to give products according to the Markownikoff rule, i.e. the nucleophile A^- ends up at the ring carbon atom where intermittent electron deficiency is best tolerated.[2]

We have studied the behaviour of some cyclopropanes (**1**) with geminal electron-withdrawing substituents. Our object was (i) to study the direction of ring cleavage and (ii) to see how the protonated starting material behaved towards acids with anions of low nucleophilic capacity. The acids used were TFA and anhydrous perchloric acid ($HClO_4$).



Scheme 1. **1c** **11**



1

a R′ = R″ = Z = H, X = Y = CO_2Me
b R′ = R″ = Me, X = Y = Co_2Me, Z = H
c R′ = R″ = Me, X = Y = Co_2Me, Z = MeO
d R′ = R″ = Me, X = Y = Co_2Me, Z = CN
e R′ = R″ = Me, X = Y = Co_2Me, Z = Ph
f R′ = Me, R″ = H, X = Y = CO_2Me, Z = Ph
g R′ = R″ = Me, X = CN, Y = CO_2Me, Z = MeO
h R′ = R″ = Me, X = CN, Y = CO_2Me, Z = H
i R′ = R″ = Me, X = Y = CN, Z = H
j R′ = R″ = Me, X = Y = Z = CN
k R′ = R″ = Me, X = Y = CN, Z = Ph

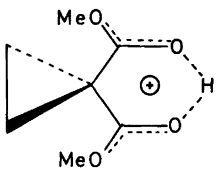
From Table 1 it can be seen that the presence of geminal cyano substituents decreases the reactivity drastically. This observation can be rationalised by looking at the first step of the reaction, which obviously must be the protonation.

In principle, a substituted cyclopropane molecule may be protonated in two ways, viz. at the substituent or at the ring, forming either edge- or corner-protonated rings.[2] Deuterium incorporation in the methyl groups of 2-methyl-2-butenoic acid (tiglic acid) formed by treatment of 1- and 2-methylcyclopropane-carboxylic acids with 98 % D_2SO_4 indicated primary deuteriation of the cyclopropane ring.[3] On the other hand, cyclopropane-1,1-dicarboxylic acid treated with 98 % D_2SO_4 gave α-carboxy-γ-butyrolactone with deuterium only in the α-position, an observation easily explained by primary deuteriation of the carboxylic substituent (*vide infra*).[3] We intend to show (*vide infra*) that some of the cyclopropanes employed in this study give olefinic products without any incorporation of deuterium when decomposed in TFA-*d*. It is thus very likely that in cyclopropanes with geminal electron-withdrawing groups the ring is too deactivated to be protonated, and that the primary protonation takes place on the substituents. Judging from the measured pK'_As of their conjugate acids [$pK_{A(RCN)} \sim -(10\text{–}12)$,[4] $pK_{A(RCOOR')} \sim -(6\text{–}8)$[5]], aliphatic nitriles are protonated less easily than esters or carboxylic acids. In the perchloric acid experiments ($pK_A \sim -20$) one would expect that even the dinitriles should be completely protonated. However, when discussing the further fate of the protonated species, their kinetic acidities, i.e. the ion life-times, must be taken into consideration. If the protonated diester has a longer life-time, decomposition may take place in competition with deprotonation. Intramolecular hydrogen bonding may be important in lowering the kinetic acidities of the protonated diesters, as shown in structure **2**. The structural similarity to the monoanion **3** of cyclopropane-1,1-dicarboxylic acid is obvious. The thermodynamic stability of **3** is documented by the very low second ionisation constant for this acid ($K_1/K_2 = 4.06 \times 10^5$ compared to

Table 1. Decomposition of cyclopropanes **1** in acids. Cleavage mode and yield of decomposition products.[a]

Cpd.	Cleavage mode	TFA	$HClO_4$
1a	–	N.r.[b]	**8a**(92)
1b	1.3	**5b**(8), **8b**(56), **13**(24)	**8b**(87)
1c	1.2	**11**(92)	N.c.[c]
1d	1.3	N.r.[b]	**1d**(13), **8d**(72)
1e	1.3	**5e**(27), **6e**(58)	**8e**(87)
1f	1.2	**10f**(87)	N.c.[c]
1g	1.2	**11g**(92)	N.c.[c]
1h	1.3	N.r.[b]	**1h**(48), **8h**(19), **14**(23)
1i	–	N.r.[b]	N.r.[b]
1j	–	N.r.[b]	N.r.[b]
1k	–	N.r.[b]	N.r.[b]

[a]Yields in %. [b]N.r.: No reaction. [c]N.c.: Not checked.



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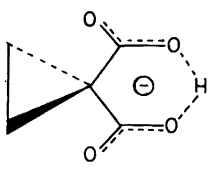


3

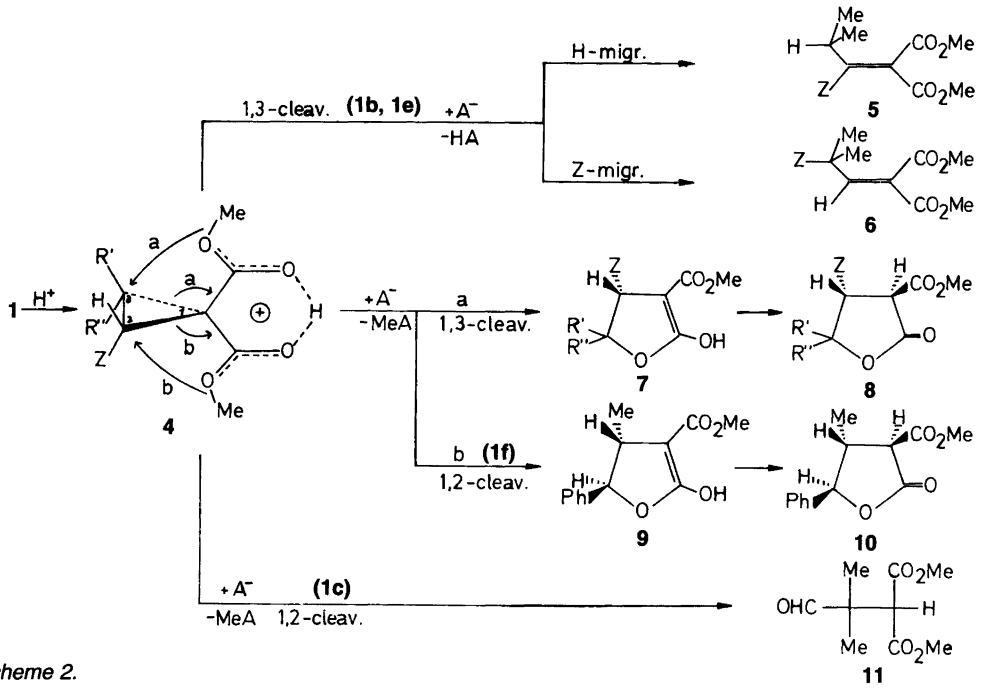
$4.5–7.1\times10^2$ for the four-, five- and six-membered cyclic 1,1-dicarboxylic acids and 7.3×10^3 for malonic acid).[6] That such intramolecular hydrogen bonds are important in this connection is also indicated by the failure of *trans*-cyclopropane-1,2-dicarboxylic acid to decompose or to become deuteriated in 98 % D_2SO_4 at 100 °C.[3] We also found that the cyano ester **1h** reacted very sluggishly in $HClO_4$ and was completely stable in TFA.

The further fate of protonated diesters **1a–f** is outlined in Scheme 2. Whether 1,2- or 1,3-cleavage occurs will certainly depend on the substituents at C2 and C3.

At this point it should be pointed out that in each of our experiments, ^1H NMR spectra of the crude product indicated that only *one* of the possible cleavage modes was followed. This means that a maximum of ~10 % of the crude products *could* have been cleaved in the competing mode (NMR signals hidden in the spectral noise), as also confirmed by capillary GLC analysis.

The experimental results do not warrant any definite conclusion with regard to the finer details of the decomposition routes; i.e. whether bond-breaking precedes bond-making (a carbocation mechanism) or *vice versa* (by a more concerted mechanism). The ring opening of **1c** (Scheme 1) to give the aldehydo ester **11** (and the corresponding ring opening of **1g**) could be explained by a preceding 1,2-bond cleavage to give a carbocation effectively resonance-stabilized by the methoxy group, the reaction sequence being terminated by the removal of the methoxy methyl group by the TFA anion. In a more synchronous way, the TFA anion could act as a nucleophile in a S_N2-like process with **11** as the leaving group.

As mentioned above, decomposition of some cyclopropanes (**1b** and **1e**) in TFA leads to olefinic products. Similar rearrangement was observed when 5-isopropylbicyclo[3.1.0]hexan-2-one in acidic solution gave 4-isopropyl-2-cyclohexen-1-one.[7]



Scheme 2.

No deuterium was found in the olefinic products when TFA-*d* was used (proven by MS analysis). Thus, the isopropyl hydrogen in **5** and the vinylic hydrogen in **6** must have present in the starting material. The formation of these 1,3-cleavage products may be explained by a hydride/phenyl anion shift to a C3 carbocation, or through migration of these groups concerted with the 1,3-bond cleavage.

In contrast to the above decompositions where concerted mechanisms are stereoelectronically conceivable, the stereospecific lactone formation seems more intricate. The lactones **8** ($Z \neq H$) formed by 1,3-cleavage of cyclopropanes **1d** and **1e** (in $HClO_4$) have the hydrogens in the α- and β-positions *trans* to each other, as demonstrated by the rather large vicinal coupling constants (11–13 Hz)[8] and by their failure to epimerise, although complete deuterium exchange took place within minutes in conc. D_2SO_4. Thermodynamically controlled "ketonisation" of enol **7** explains the stereospecificity; hence, no information regarding the timing of bond-making/-breaking is available from these experiments.

Cyclopropane **1f** has the *trans* configuration.[9] In contrast to the formation of lactones **8**, where the ring closure takes place at a non-chiral carbon atom, lactone **10** has a chiral atom in the γ-position (Scheme 2, path b). The *trans* relation of the methyl and the phenyl groups is retained after the ring transformation. Stereoelectronically, a concerted bond-making/bond-breaking mechanism seems highly unlikely. Thus, one is left with two possible mechanisms:

(i) the time lag between bond-breaking (to give a carbocation at C2) and the bond-making is shorter than the time of rotation around the C2–C3 bond (kinetic control), the *trans*-to-*cis* rotational barrier being increased for steric reasons;
(ii) a thermodynamically controlled equilibrium is involved at a later stage, the *trans* form being most stable (Scheme 3).

Again, the "ketonisation" of enol **9** gives the thermodynamically more stable configuration around the Cα–Cβ-bond in lactone **10**.

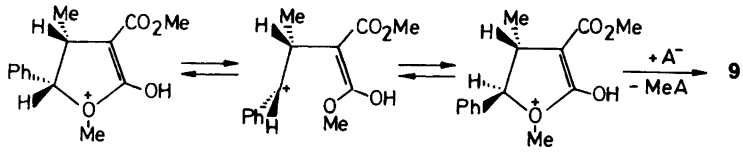
Of the two phenyl-substituted compounds **1e** and **1f**, **1e** undergoes 1,3-cleavage while **1f** is cleaved at the 1,2-bond. This observation is analogous to solvolysis reactions where the reactivity order is: tertiary alkyl halides (cf. C3 in **1e**) > secondary allyl halides (cf. C2 in **1e** and **1f**) > secondary alkyl halides (cf. C3 in **1f**).[10]

When cyclopropane **1c** was exposed to acidic aluminium oxide, lactone **12** was formed (Scheme 4). The lack of a nucleophile (with the exception of basic sites on the alumina surface) leads to ring enlargement instead of the ring opening observed in TFA (to give **11**).

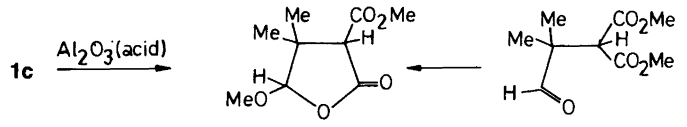
As described in the Experimental section, the aldehydo ester **11** gives the same lactone **12** upon standing neat for several weeks. Since this ring closure must involve a methoxy group migration which could be inter- or intramolecular in nature, equal amounts of **11** and its deuterium analogue (having CD_3 instead of CH_3 in the ester groups) were mixed and left for several weeks. MS analysis [chemical ionisation (CI)] showed that three lactones were formed: **12**: **12**-d_3: **12**-d_6 = 0.98: 2.0: 1.08, i.e. in a nearly statistical ratio (1:2:1); this indicates an intermolecular migration concerted with lactone formation, as intramolecular migration should give only **12** and **12**-d_6 in equal amounts.

However, considering the long reaction time in the above reaction, one cannot rule out a preceding lactone formation followed by an acid-catalysed exchange of the alkoxy groups attached to the lactone ring, either autocatalysed, involving the α-proton of **12**, or "externally" catalysed by the acidic proton of **11** to give the final deuterium distribution (*vide supra*) (Scheme 5.)

In order to obtain some more information regarding intra- vs. intermolecular migration, three experiments were initiated: (I) equimolar amounts of aldehydoesters **11** and **11**-d_6, (II) equimolar amounts of lactones **12** and **12**-d_6, and



Scheme 3.

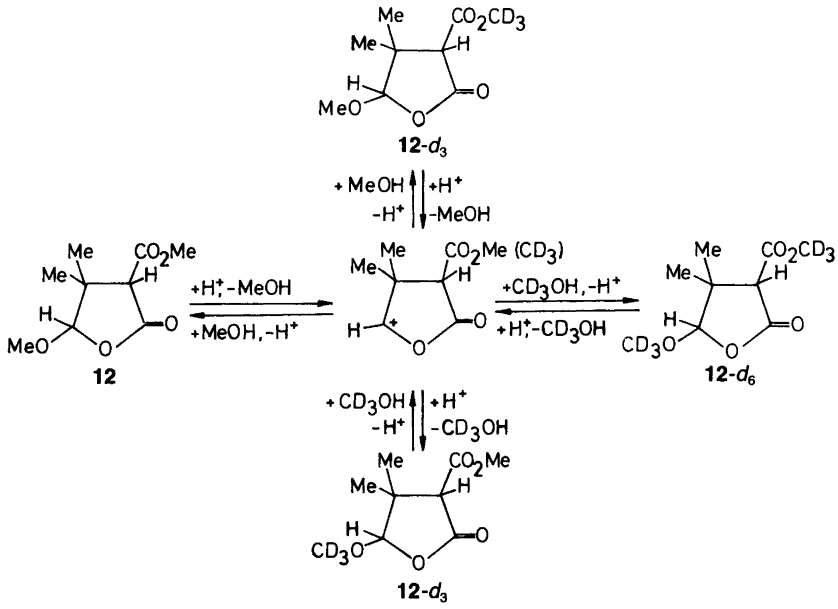


Scheme 4.

(III) equimolar amounts of **12** and **12**-d_6 to which was added some aldehydo ester **11**, were kept at 55 °C (lactone **12** has m.p. 54 °C) for several weeks. Samples were withdrawn and examined by GLC-MS. Electron-impact mass spectrometry (EIMS) gave no molecular ion, and chemical ionisation (CIMS) was therefore used. Progress of the transformation of aldehydo esters **11** to lactones **12** [Experiment (I)] was followed by examining the mass chromatograms (Table 2). However, separation of the different aldehydo esters **11**, **11**-d_3 and **11**-d_6 or of the different lactones **12**, **12**-d_3 and **12**-d_6 was not achieved under the chromatographic conditions used. Each chromatographic peak was scanned 20–50 times. The compounds (**11** and **12**) with highest deuterium content consistently had the lowest retention time. By computerised addition (and finally normalisation) of the ion currents representing *m/z* 203, 206 and 209 (MH^+ of both **11**'s and **12**'s) in each scan, the relative content of the three aldehydo esters, viz. lactones, could be estimated; results are given in Table 2.

Examination of Table 2 permits the following conclusions: (i) Alkoxy exchange between the aldehydo esters **11** and **11**-d_6 is negligible, (ii) alkoxy exchange (autocatalysed or "externally" catalysed) between lactones **12** and **12**-d_6 is a rather slow process, and (iii) the nearly random distribution (**12**: **12**-d_3: **12**-d_6) after half-way ring formation (7 days) clearly indicates that a complete scrambling of the methoxy groups takes place intermolecularly concerted with ring formation.

Whether the alkoxy exchange is bimolecular or of higher molecularity is a question of a more philosophical nature. In solution chemistry, the occurrence of reactions of molecularity higher than two is rather unlikely. In the condensed phase with local molecular order approaching that of a crystalline structure, a "domino" effect might be possible (Scheme 6).



Scheme 5.

Scheme 6.

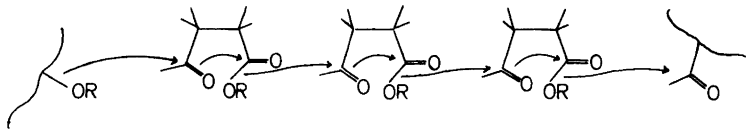


Table 2. Mass spectrometric (GC–CI) monitoring of isomerisation of aldehydo ester **11** and of lactone **12**.[a]

Sample[b]	Time	0		7d		13d		35d		43d		52d	
	Cpd.[c]	A	L	A	L	A	L	A	L	A	L	A	L
	% A,L[d]	100	0	53	47	35	65	9	91	0	100	0	100
	MH^+												
I	203	89		89	56	95	51	96	50		49		51
	206	0		9	100	9	100	8	100		100		100
	209	100		100	59	100	54	100	53		54		54
II	203		100		100		100		100		81		100
	206		0		9		30		38		100		92
	209		100		98		92		88		77		99
III	203		100		100		100		100		100		100
	206		0		16		39		57		80		82
	209		90		80		74		72		73		77

[a]Description of experiments, see text. [b]I: 100 mg **11** + 100 mg **11**-d_6; II: 40 mg **12** + 40 md **12**-d_6; III: As for II, + 10 mg **11**. [c]A: Aldehydo ester **11**; L: Lactone **12**. [d]Chromatographically estimated.

Experimental

General. Melting points (uncorrected) were determined on a Mettler FP61 melting point apparatus. IR spectra were recorded on a Shimadzu IR 435 spectrophotometer, NMR spectra on JEOL JNM-PMX 60Si and/or JEOL FX 90Q spectrometers and mass spectra on a VG-Micromass 7070H instrument equipped with a Hewlett Packard 5710A gas chromatograph (capillary columns). Gas chromatography was performed on a Carlo Erba HRGC 5300 chromatograph equipped with a LDC/Milton Roy CI-10B integrator, and employing a Chrompack CP Sil 5CB, 26 m long capillary column.

Syntheses of cyclopropanes **1**. The following compounds were prepared according to known methods: Dimethyl cyclopropane-1,1-dicarboxylate (**1a**),[11] dimethyl 2,2-dimethyl-cyclopropane-1,1-dicarboxylate (**1b**),[12] dimethyl 3,3-dimethyl-2-methoxycyclopropane-1,1-dicarboxylate (**1c**),[1] dimethyl 2-cyano-3,3-dimethyldicyclopropane-1,1-dicarboxylate (**1d**),[12] methyl 1-cyano-2-methoxy-3,3-dimethylcyclopropanecarboxylate (**1g**),[13] 2,2-dimethylcyclopropane-1,1-dicarbonitrile (**1i**),[12] 2-cyano-3,3-dimethylcyclopropane-1,1-dicarbonitrile (**1j**)[13] and 3,3-dimethyl-2-phenylcyclopropane-1,1-dicarbonitrile (**1k**).[14]

Dimethyl 3,3-dimethyl-2-phenylcyclopropane-1,1-dicarboxylate (**1e**) was synthesized by the reaction of dimethyl diazomalonate[15] with 2-methyl-1-phenyl-propene.[16] Yield 42%. B.p. 103–105 °C/0.1 mmHg. Anal. $C_{15}H_{18}O_4$: C,H. MS[70 eV, *m/z* (% rel.int.)]: 262 (7, M), 247 (22 [M-Me]), 198 (100 [M-2MeOH]). Mol.wt.: obs. 262.1174, calc. for $C_{15}H_{18}O_4$ 262.1205. ^{1}H NMR (60 MHz, CCl_4): δ 7.13 (5H, br.s.), 3.75 (3H, s), 3.60 (3H, s), 2.97 (1H, s), 1.39 (3H, s), 1.30 (3H, s). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 169.6 and 167.6 (C=O), 134.8 (C1′), 129.7 and 128.1 (C2′–C5′), 126.8 (C6′), 52.5 and 51.8 (O–CH_3), 43.7 (C1), 40.0 (C2), 31.3 (C3), 24.1 and 18.8 (2 Me). IR (film): 3055 (w), 3025 (w), 2948 (m), 1728 (s) cm^{-1}.

Dimethyl 3-methyl-2-phenylcyclopropane-1,1-(**1f**) *dicarboxylate* was prepared by reaction of dimethyl (2-bromo-1-phenylpropylidene)-malonate[17] with sodium borohydride.[12] Yield 78%. B.p. 98–100/0.01 mmHg. Anal. $C_{14}H_{16}O_4$: C,H. ^{1}H NMR (60 MHz, CCl_4): 7.11 (5H, br.s), 3.72 (3H, s), 3.30 (3H, s), 2.95 (1H, d, J = 7.8 Hz), 2.2–2.7 (1H, m), 1.28 (3H, d, J = 7.3 Hz). IR (film): 1730 cm^{-1}.

Methyl 1-cyano-3,3-dimethylcyclopropanedicarboxylate (**1h**) was prepared from methyl 2-cyano-3-methyl-2-butenoate (prepared by Knoevenagel condensation of acetone with methyl cyanoacetate) using dimethyl sulfoxonium methylide as cyclopropanating agent.[18] Yield 50%. B.p. 84–86 °C/10 mmHg. Anal. $C_8H_{11}NO_2$: C,H. MS[70 eV, *m/z* (% rel.int.)]: 152(5 [M−H]), 138(14 [M−Me]), 121(100, [M−MeOH]). ^{1}H NMR (60 MHz, CCl_4): δ 3.78 (3H, s), 1.77 (1H, d, J = 5.0 Hz), 1.47 (3H, s), 1.44 (1H, d, J = 5.0 Hz), 1.28 (3H, s). IR(film): 3100 (vw), 2952 (s), 1735 (s) xm^{-1}.

Decomposition of cyclopropanes **1**. *General.* Five mmol of the substrates were used in the decomposition experiments, and the progress of the reaction was monitored by ^{1}H NMR. Reaction temperature was 25 °C in the trifluoroacetic acid [TFA (50 ml)] and 50 °C in the perchloric acid ($HClO_4$) experiments, and nitrogen atmosphere was used. Anhydrous $HClO_4$ was prepared in the following way:[19] Silver perchlorate monohydrate (FLUKA AG 5 mmol) was suspended in benzene (100 ml) and the suspension was heated under reflux for 2 h using a Dean and Stark water separator to remove the hydrate water. The anhydrous $AgClO_4$ dissolved, and after cooling, hydrogen chloride was bubbled into the solution for 20 min to precipitate silver chloride. After purging with nitrogen for 2 h the perchloric acid solution was transferred to the decomposition flask through a tube fitted with a sintered glass disc.

Work-up procedure. TFA. The solution was concentrated using a rotary evaporator (Büchi), water and ether were added, the dried ($MgSO_4$) ether phase evaporated and the residue chromatographed on silica columns.

$HClO_4$. Saturated sodium bicarbonate solution was added, the dried ($MgSO_4$) benzene phase evaporated and the residue chromatographed on silica columns.

Products. The residues were analyzed by capillary gas chromatography. The total yields of the products described below were always close to 90%.

Results (reaction time). **1a**. *TFA* (>7 days): No reaction.

$HClO_4$ (24 h): Only α-methoxycarbonyl-γ-butyrolactone (**8a**) isolated (~92%).

1b. *TFA.* (8 h): α-Methoxycarbonyl-γ,γ-dimethyl-γ-butyrolactone (**8b**) (56%);[20] methyl trifluoroacetate (52%, GLC); dimethyl (2-methylpropylidene) malonate (**5b**) (8%); dimethyl (2-methyl-2-trifluoroacetoxypropyl)malonate (**13**) (24%): Anal. $C_{11}H_{15}FO_4$: C,H. ^{1}H NMR (60 MHz, CCl_4): δ 3.67 (6H, s), 3.40 (1H, t, J = 7.2 Hz), 2.41 (2H, d, J = 7.3 Hz), 1.57 (6H, s). ^{13}C NMR (22.5 MHz, CCl_4): δ 168.2 (2xC=O), (C2), 52.0 (2xOMe), 46.7 (−C−H), 39.1 (Cl), 25.1 (2xMe). IR (film): 1785 (s), 1760 (s), 1745 (s) cm^{-1}.
$HClO_4$ (6 h): α-Methoxycarbonyl-γ-γ-dimethyl-γ-butyrolactone (**8b**) (87%).[20]

1c. *TFA* (6 h): Dimethyl (1-formyl-1-methylethyl)malonate (**11**)[21] (92%), and methyl trifluoroacetate (GLC).

1d. *TFA* (>3 days): No reaction.

$HClO_4$ (20 h): Unreacted starting material (13%); α-methoxycarbonyl-β-cyano-γ,γ-dimethyl-γ-butyrolactone (**8d**) (72%). M.p. 86–7 °C. Anal. $C_9H_{11}NO_4$: C,H. ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.07 (1H, d, J = 11.0 Hz), 3.91 (3H, s), 3.72 (1H, d, J = 11.0 Hz), 1.68 (3H, s), 1.60 (3H, s). ^{13}C (22.5 MHz, $CDCl_3$): δ 166.4 and 165.4 (2xC=O), 115.6 (C≡N), 82.7 (C−α), 54.0 (OMe), 50.6 (C−β), 39.9 (C−γ), 27.5 and 24.9 (2xMe). MS[70 eV, *m/z* (% rel.int.)]: 182(3 [M−Me]), 155(44), 127(83), 43(100). IR(KBr): 2980(w), 2960(m), 2895(m), 2250(m), 1778(s), 1726(s) cm^{-1}.

1e. *TFA* (20 h). Dimethyl (2-methyl-2-phenylpropylidene)malonate (**6e**) (58%). ^{1}H NMR (60 MHz, CCl_4): δ 7.27 (5H, br.s), 7.12 (1H, s), 3.73

(3H, s), 3.43 (3H, s), 1.52 (6H, s); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 166.3 and 164.8 (2xC=O), 155.1 (Cl), 145.9, 128.3, 126.6 and 126.1 (C-arom), 126.6[=*C*$(CO_2Me)_2$, 52.4 and 51.9 (2xOMe), 41.6 (C2), 28.7 (2xMe). MS[70 eV, *m/z* (% rel.int.)]: 262 (22 [M]), 247 (6 [M-Me]), 198 (100 [M-2 MeOH]). IR (CCl_4): 2948 (m), 1733 (s), 1639 (w) cm^{-1}; Dimethyl (2-methyl-1-phenylpropylidene) malonate (**5e**) (27 %). ^1H NMR (60 MHz, CCl_4): δ 7.0–7.6 (5H, m), 3.63 (3H, s), 3.53 (1H, m, J = 7.5 Hz), 3.72 (3H, s), 3.38 (3H, s), 1.01 (6H, d, J = 7.5 Hz). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 165.5 and 165.4 (2xC=O), 164.3 (Cl), 136.4, 127.9, 127.6 and 127.5 (arom. C), 125.5[=*C*(CO_2Me)], 52.2 and 51.7 (2xOMe), 32.0 (C2), 20.7 (2xMe). MS[70 eV, *m/z* (% rel.int.)]: 262 (5[M]), 247 (2 [M-Me]), 198 (100 [M-2MeOH]. IR(CCl_4): 2945 (m), 1729(s), 1617 (m) cm^{-1}.

$HClO_4$ (10 h): γ,γ-Dimethyl-α-methoxycarbonyl-β-phenyl-γ-butyrolactone (**8e**) (87 %).[20]

1f. *TFA* (2 days): β-Methyl-α-methoxycarbonyl-γ-phenyl-γ-butyrolactone (**10f**) (87 %). M.p. 79–81 °C. Anal. $C_{13}H_{14}O_4$: C,H. ^1H NMR (60 MHz, CCl_4): δ 7.28 (5H, b.s), 4.75 (1H, d, J = 10.5 Hz), 3.74 (3H, s), 3.25 (1H, d, J = 12.8 Hz; exchangeable in D_2O), 3.0–2.5 (1H, m), 1.14 (3H, d, J = 7.2 Hz). ^{13}C NMR (22.5 MHz, CCl_4): δ 168.7 and 166.7 (2xC=O), 136.9, 128.5 and 126.3 (arom. C), 85.5 (γ−C), 54.4 (OMe), 52.2 (α−C), 43.7 (β−C), 14.4 (Me). IR(KBr): 2965 (m), 2920 (m), 1775 (s), 1745 (s) cm^{-1}; Methyl trifluoroacetate (GLC).

1g. *TFA* (12 h): Methyl 2-cyano-3,3-dimethyl-4-oxobutanoate (**11g**, 92 %). B.p. 66–68 °C/0.01 mmHg. Anal. $C_8H_{11}NO_3$: C,H. ^1H NMR (60 MHz, CCl_4): δ 9.38 (1H, s), 3.83 (1H, s), 3.78 (3H, s), 1.32 (3H, s), 1.26 (3H, s). IR (CCl_4): 2950 (m), 2790 (w), 2710 (w), 2240 (m), 1755 (s), 1720 (s); Methyl trifluoroacetate (GLC).

1h. *TFA* (5 days): No reaction.

$HClO_4$ (20 h): Unreacted starting materials (48 %); α-methoxycarbonyl-γ,γ-dimethyl-γ-butyrolactone (**14**) (23 %);[20] α-cyano-γ,γ-dimethyl-γ-butyrolactone (**8h**) (19 %): ^1H NMR (60 MHz, $CDCl_3$), ABX system: 3.94 (H_X), 2.59 (H_B), 2.42 (H_A), J_{AX} = 11.7 Hz, J_{BX} = 7.8 Hz, J_{AB} = 12.8 Hz, 1.60 (3H, s), 1.43 (3H, s). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 167.4 (C=O), 115.2 (C≡N), 84.8 (γ−C), 39.0 (β−C), 32.5 (α−C), 26.4 and 27.8 (2xMe). MS[70 eV, *m/z* (% rel.int.)]: 124 (100 [M-Me]), 106 (20). IR(film): 2975 (m), 2911 (m), 2251 (w), 1774 (s) cm^{-1}.

Ring closure of dimethyl (1-formyl-1-methylethyl) malonate (**11**). When pure samples of **11** were left for several weeks, crystals were formed which were identified as γ-methoxy-α-methoxycarbonyl-β,β-dimethyl-γ-butyrolactone (**12**).[21] When cyclopropane **1c** was applied on a chromatography column packed with acidic aluminium oxide (Woelm) and left for 1 h before elution, the same lactone was formed in 25 % yield. When a mixture of equal amounts of **11** and its deuteriated analogue (CD_3 instead of CH_3 in the ester groups) was left for several weeks, mass spectrometry (chemical ionisation, isobutane as reagent gas) showed relative abundances of 46 % (*m/z* 203, MH^+ of non-deuteriated lactone), 100 % (*m/z* 206, MH^+ of trideutero lactone) and 54 % (*m/z* 209, MH^+ of hexadeutero lactone).

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