Gas-Phase Kinetics of the Thermal 1-Alkoxy-1-vinylcyclopropane to 1-Alkoxy-1-cyclopentene Rearrangement

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The title studies have been carried out with both 1-vinyl-1-cyclopropyl methyl ether (**1-OMe**) and 1-vinyl-1-cyclopropyl ethyl ether (**1-OEt**) in the temperature ranges 274.6 − 324.5 and 273.6 − 323.0 °C, respectively. Both reactions predominantly give the vinylcyclopropane-cyclopentene (VCP-CP) rearrangement products 1-cyclopenten-1-yl methyl ether (**2-OMe**) and 1-cyclopenten-1-yl ethyl ether (**2-OEt**). Additionally, **2-OEt** eliminates ethene (**3**) in a consecutive reaction at a lower reaction rate compared with the VCP-CP rearrangement. The rearrangements obey first-order kinetics and have been shown to be homogeneous, pressure-independent reactions with the following Arrhenius equations:

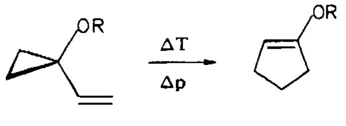
1-OMe: $\lg(k/s^{-1}) = (13.89 \pm 0.23) - (191.30 \pm 2.55\ \mathrm{kJ\,mol^{-1}})/RT\ln 10$

1-OEt: $\lg(k/s^{-1}) = (13.77 \pm 0.01) - (188.80 \pm 1.85\ \mathrm{kJ\,mol^{-1}})/RT\ln 10$

The Arrhenius parameters represent reliable values for general 1-vinyl-1-cyclopropyl alkyl ether → 1-cyclopenten-1-yl alkyl ether (**1-OR** → **2-OR**) rearrangements within a large temperature interval in the gas phase. The results support a mechanism proceeding via a diradical. The stabilizing effect of methoxy substitution is discussed.

The feasibility of the vinylcyclopropane-to-cyclopentene (VCP-CP) rearrangement in preparative organic synthesis has become a subject of major interest during the last three decades[2−4)]. This has led to a variety of kinetic investigations of the reaction, carried out by numerous workers mainly on non-heteroatom-substituted vinylcyclopropanes[5−16)]. The facilitation of the rearrangement by donor substituents on the vinylcyclopropane moiety, first discovered and documented by kinetic measurements performed by Richey et al. for 1- and 2-methoxy-[17a)] and 2-dimethylamino[17c)]-substituted VCPs and later confirmed by Trost et al. with 1-trimethylsiloxy-substituted VCPs[18)], has proved to be of great importance in modern synthetic applications[19,20)].

1-OMe has previously been studied under gas-phase conditions by Richey et al. in the rather small temperature interval (ΔT) 263 − 287 °C and at pressures (Δp) ranging from 20 to 100 Torr[17a)]. Neither in this nor in other reports on donor-substituted VCP-CP rearrangements[17c,18)] are details described indicating as to whether the investigated reactions have been probed for their homogeneity and pressure independence. Due to this deficiency and in view of our growing interest in donor-substituted VCPs as useful synthetic tools[20)], we have undertaken a thorough kinetic investigation of two 1-alkoxy-1-vinylcyclopropanes **1-OR** (R = Me, Et).



1-OR **2-OR**

1-OMe: ΔT = 274.6-324.5 °C; Δp = 14-33 torr

1-OEt: ΔT = 273.6-323.0 °C; Δp = 18-28 torr

Preparation of 1-Alkoxy-1-vinylcyclopropanes 1-OR

Alkoxyvinylcyclopropanes **1-OR** have been prepared in four consecutive steps. Cyclization of ethyl 3-chloropropionate to 1-ethoxy-1-(trimethylsiloxy)cyclopropane[21)] and methanolic cleavage of the trimethylsilyl protecting group gives 1-ethoxy-1-cyclopropanol[22)]. The cyclopropanone hemiacetal has been treated with methylmagnesium iodide and the product vinylated with vinylmagnesium bromide to yield **1-OH** according to similar procedures of Wasserman et al.[23)]. By deprotonation of **1-OH** with methyllithium (MeLi) in ether at −78 °C and subsequent quenching of the resulting lithium alkoxide with trialkyloxonium tetrafluoroborates (prepared by methods of Meerwein[24)]) **1-OH** is quantitatively converted to **1-OR** (analogous alkylations can be performed by treatment of the alkoxides with alkyl trifluoromethanesulfonates). Repeated preparative-scale gas chromatography has been required to purify vinylcyclopropyl ethers **1-OR** to purity grades >99.99%, which are desirable for quantitative kinetic investigations.

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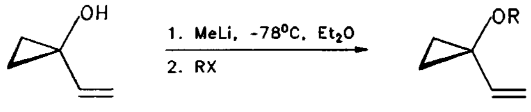


R = Me, Et

1-OH X = $R_2O^+BF_4^-$, SO_3CF_3 **1-OR**

The VCP-CP rearrangement products **2-OR** have been prepared independently and used as authentic product samples during the kinetic analyses. Acetalization of cyclopentanone to cyclopentanone dialkyl acetals and subsequent acidic elimination of alkanol gave 1-cyclopenten-1-yl alkyl ethers **2-OR** in high yields[25]. **2-OMe** and **2-OEt** have further been purified by preparative-scale gas chromatography.

Kinetic Measurements

The kinetic studies were carried out in an apparatus similar to that used in earlier studies, consisting of a hexamethyldisilazane-(HMDS-)conditioned static reaction vessel connected to a vacuum line[26a–d]. The reaction vessel can be replaced by a packed vessel with a surface-to-volume ratio (S/V) of approx. 10 cm^{-1}, in which the reactions have been tested for surface-catalytic activity.

Each pyrolysis has been performed with highly diluted (N_2) samples of **1-OR** from previously prepared master mixtures by using cyclohexane (CH) as an inert internal standard. The master mixtures consisted of approx. 1.24% **1-OMe** (0.9% CH), and 1.22% **1-OEt** (0.49% CH), respectively. Before each run a blank sample of the pure reactant mixture was analyzed gaschromatographically and compared with the reactant/CH/product mixture of the reaction run. This procedure enabled checks to be performed on the mass balance during reaction runs. Thus, in the study of **1-OMe** apparent mass losses of up to 40% have been found by gas chromatographic (GC) analysis (30-min run at 314°C and 75.4% conversion to **2-OMe**). This effect, however, has been traced to product sampling losses rather than to unknown side reactions. The reason for this problem may be attributed to the low vapour pressure of the products **2-OR**. Vapour pressure measurements of both pure reactants **1-OR** and products **2-OR** show the latter to be significantly less volatile (Table 1). Eventually, the only material loss has been found to be due to a loss of product **2-OMe** on the basis of the following evidence: firstly, ratios of **1-OMe** to CH in blanks are constant with a total pressure variation and do not decrease over long times. Secondly, in reaction runs apparent mass losses increase steadily with increasing reaction time (i.e. as the proportion of **2-OMe** rises). Thirdly, pyrolyses of **1-OMe** at low conversions to **2-OMe** give complete mass recoveries within experimental error. If neat **2-OMe** is left in the reaction vessel under the reaction conditions even higher product losses occur in the subsequent GC analysis than for the dilute reaction mixtures.

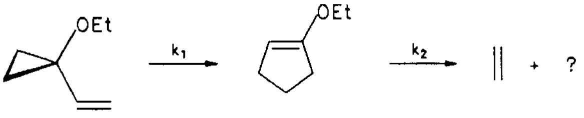
Thus, in the study of **1-OMe**, because mass losses are due to the product alone, the quantitative kinetics have been based on reactant disappearance. Subsequent to the study of **1-OMe**, by alteration of the sampling and analysis conditions, mass loss problems have been avoided for **1-OEt** so that material recovery has been complete within experimental error, in spite of the even lower vapour pressure of **2-OEt**.

The generation of **2-OMe** from **1-OMe** is accompanied by minor production of some unidentified volatile products (similar observations have been made by Richey et al.[17a)]). The amount of these products, the main one of which elutes at 1.66 min (for GC conditions see experimental section) never exceeded 4% based on peak area.

Table 1. Vapour pressures of **1-OR** and **2-OR** at room temperature

Compound	1-OMe	1-OEt	2-OMe	2-OEt
Pressure [Torr]	37	18	7	3

In the study of **1-OEt**, considerable quantities of ethene (**3**) have been detected in addition to the major product **2-OEt**. **3** has been identified by a comparison of its retention time with that of an authentic sample. Time evolution studies (see below) have revealed that **3** was a secondary product. This has been confirmed by direct pyrolysis of authentic **2-OEt**. Direct formation of **3** from **1-OEt** is ruled out by an examination of the ratio [**3**]/[**2-OEt**] which grows steadily with time and extrapolates to zero at the start of the reaction (Table 3). In fact, the product evolution (Figure 1) follows the typical pattern of a pair of consecutive unimolecular reactions with **2-OEt** growing to a maximum before declining again.



1-OEt **2-OEt** **3**

$k_1 > k_2$

There has been no problem with mass recovery in this system, and the calibration factor employed for **3** (3.5 relative to **2-OEt**) is typically that expected for FID response.

The remaining product(s) apart from **3** formed in the decomposition of **2-OEt** could not be identified. On the basis of the retro-ene decomposition mechanism of vinyl ethers[27a–c] the additional product should be cyclopentanone. Unfortunately, the employed GC column has proved to be unsuitable for its detection, since an authentic sample of cyclopentanone and the consecutive product(s) formed by pyrolysis of **2-OEt** both revealed very long (non-identical) and variable retention times. This product identity has not been further pursued, since the main objective has been the determination of the kinetics of step (1). It should nevertheless be pointed out that this type of consecutive reaction does not occur with the non-vinylic ether 4-cyclopenten-1-

yl ethyl ether produced under similar conditions by VCP-CP rearrangement of 2-vinyl-1-cyclopropyl ethyl ether[28].

(i) *Time Dependence:* Six to eight pyrolyses have been performed at each temperature with selected reaction times corresponding to total conversions of **1-OR** between 1.4 and 93.4%. The initial total reaction pressures varied between 14 and 33 Torr (**1-OMe**) and 18−28 Torr (**1-OEt**), i.e. actual reactant partial pressures of 0.17−0.41 Torr (**1-OMe**) and 0.22−0.34 Torr (**1-OEt**). The observed conversions and product variations with time are shown in Tables 2 and 3 for similar temperatures.

Table 2. Pyrolysis of **1-OMe** at 274.6°C. Conversion of **1-OMe** with time

Time [min]	60	120	240	315	480	600	900
1-OMe (%)	9.16	21.41	43.98	55.58	70.70	79.45	90.41

Table 3. Pyrolysis of **1-OEt** at 273.6°C. Product variation and conversion of **1-OEt** with time[a]

Time [min]	**1-OEt**	Total (%) **2-OEt**	**3**	Ratio **3/2-OEt**
120	79.90	16.97	3.13	0.18
240	59.80	30.00	10.20	0.34
300	51.53	34.87	13.60	0.39
460	30.74	43.36	25.90	0.60
600	9.84	42.23	37.94	0.90
900	5.92	34.40	59.68	1.73

[a] Calculations based on average proportion of **1-OEt** in master mixtures (blank runs).

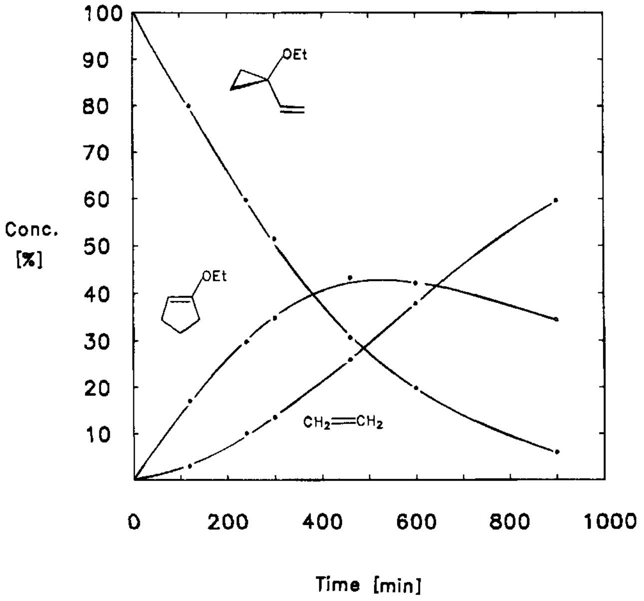


Figure 1. Pyrolysis of **1-OEt** at 273.6°C. Product variation with time

First-order graphs have been obtained by plotting the logarithm of the concentration of the remaining reactant **1-OR** (in %) vs. reaction time. A linear regression analysis (least mean-squares procedure) of the experimental data gives good linearities with absolute correlation coefficients ($|r|$) within the following limits at different temperatures:

1-OMe: $0.9995 \geqslant |r| \geqslant 0.9980$
1-OEt: $0.9998 \geqslant |r| \geqslant 0.9986$

Rate constants are obtained from the slopes of the graphs.

(ii) *Temperature Dependence:* Compounds **1-OR** have been studied at six approximately equidistant temperatures (ca. 10°C intervals) over a range of 50°C. Table 4 shows the variation of rate constants with temperature for the performed VCP-CP rearrangements.

Table 4. Rate constant variation with temperature for VCP-CP reactions **1-OR** → **2-OR**

1-OMe Temp. [°C]	$10^4\,k$ [s^{-1}][a]	**1-OEt** Temp. [°C]	$10^4\,k$ [s^{-1}][a]
274.6	0.444 ± 0.006	273.6	0.555 ± 0.014
284.4	0.947 ± 0.016	283.6	1.107 ± 0.015
293.9	1.891 ± 0.031	293.9	2.339 ± 0.046
303.5	3.414 ± 0.087	303.0	4.372 ± 0.042
314.0	7.587 ± 0.192	313.7	9.344 ± 0.090
324.5	15.063 ± 0.175	323.0	17.052 ± 0.328

[a] Error limits are standard deviations.

Very good linear Arrhenius plots are obtained by least mean-squares fittings which are shown in Figure 2. The obtained $|r|$ values are 0.9996 for **1-OMe** and 0.9999 for **2-OEt**. Table 5 contains the Arrhenius parameters obtained from the slopes and intercepts of the Arrhenius plots.

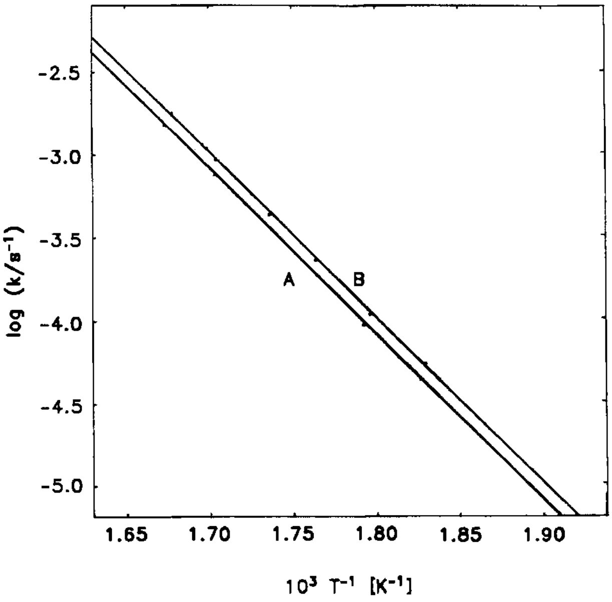


Figure 2. Arrhenius plots for thermal rearrangements of **1-OR**. − A: **1-OMe**. − B: **1-OEt**

A rough estimate of the rate constant k_2 for step (2) may be made by a simple kinetic treatment of steps (1) and (2), which shows that at the maximum of [**2-OEt**], k_1/k_2 =

Table 5. Arrhenius parameters for thermal VCP-CP rearrangements of **1-OR**

Compound	$\lg(A/\mathrm{s}^{-1})$[a]	E_a [kJ mol^{-1} (kcal mol^{-1})][a]
1-OMe	13.89 ± 0.23	191.30 ± 2.55 (45.69 ± 0.61)
1-OEt	13.77 ± 0.01	188.80 ± 1.85 (45.09 ± 0.44)

[a] Error limits are standard deviations.

[**2-OEt**]/[**1-OEt**]. An examination of the concentration vs. time figures (see e.g. Figure 1) leads to a value of k_1/k_2 of ca. 1.8 (probably reliable to ±20% but expected to be slightly temperature dependent). At 300°C, $k_1 = 3.6 \times 10^{-4}$ s^{-1} (Table 7), therefore k_2 is ca. 2.0×10^{-4} s^{-1}. This may be compared with a value of 5.0×10^{-5} s^{-1} for ethyl vinyl ether, calculated from the Arrhenius parameters for its decomposition[27a–c]. The difference factor of 4 here must be regarded as small, corresponding to a Gibbs activation energy difference ($\Delta\Delta G^{+}$) of only 6.6 kJ mol^{-1}.

(iii) *Pressure Dependence:* Although the molecules **1-OR** appear large enough for their first-order rate constants (at the measured pressures) to be well beyond the influence of the pressure-dependent "fall-off" region, a few precautionary pyrolyses have been performed for **1-OR** at elevated pressures. A 20-min run for **1-OMe** at 75 Torr and 324.5°C gives precisely the same conversion of 83.0% as under analogous conditions at 20 Torr. Also, for **1-OEt**, a 10-min pyrolysis at 74 Torr and 323.5°C gives 61.6% conversion which is – within experimental error – comparable with 59.6% conversion at 20 Torr. These results show clearly that the pressures at which kinetic measurements have been performed lie above the "fall-off" region.

(iv) *Checks for Surface-Catalysis and Radical Chain Processes:* Both VCP-CP reactions have been tested for homogeneity and radical chain processes in an HMDS-conditioned packed vessel (S/V ≈ 10 cm^{-1}) with and without an excess amount of olefin inhibitor being present (**1-OMe**: propene; **1-OEt**: *cis*-2-butene). For **1-OMe** these tests show no evidence at all either for surface effects or for the presence of radical chain components. The obtained conversions under the various reaction conditions indicated in Table 6 are consistent with a non-heterogeneous reaction in which radical chain processes can be excluded.

Nevertheless, experimental observations are not quite so clear-cut for **1-OEt**. Although the data in Table 6 present no substantial evidence for radical chain reactions taking place, a comparison of data for the packed and unpacked vessels reveals a slightly enhanced production of **2-OEt** in the packed vessel. Table 6 shows that decompositions of **1-OEt** remain well within tolerance limits of ±10% often observed in such comparisons, and that the greater production of **2-OEt** and **3** is not proportional to the actual increase of the surface in the packed vessel. Considering this and the very good first-order plots for **1-OEt**, and further recognizing the proven absence of surface catalysis for the analogous compound **1-OMe**, we believe that the data obtained justify the assumption that surface catalysis effects are also absent for **1-OEt** in the unpacked vessel.

Table 6. Product variation in packed and unpacked vessels for thermal VCP-CP reactions of **1-OR**. 10-min pyrolyses[a]

Reaction vessel	Reaction			
	1-OMe → **2-OMe** **1-OMe** (%)	**1-OEt** → **2-OEt** → **3**		
		1-OEt (%)	**2-OEt** (%)	**3** (%)
normal vessel	55.1	44.8	39.4	15.8
normal vessel[b]	57.7	46.5	38.1	15.4
packed vessel[c]	58.0	39.6	47.8	12.6
packed vessel[b,c]	57.9	39.8	48.2	12.0

[a] **1-OMe**: at 324.5°C. **1-OEt**: at 323.8°C. – [b] **1-OMe**: 12-fold excess of propene. **1-OEt**: 25-fold excess of *cis*-2-butene. – [c] S/V ≈ 10 cm^{-1}.

Discussion of Results

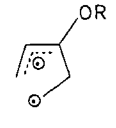
The reported results for **1-OR** reveal representative Arrhenius parameters for general 1-alkoxy-1-vinylcyclopropane (**1-OR**) → 1-alkoxy-1-cyclopentene (**2-OR**) rearrangements. Our measurements show a good agreement with Richey's results for **1-OMe**[17a] (Table 7).

Table 7. Arrhenius parameters and rate constants for selected 1-substituted VCPs in VCP-CP rearrangements

Compound	$\lg(A/\mathrm{s}^{-1})$	E_a [kJ mol^{-1}]	$10^4\,k$ [s^{-1}][a]	Ref.
1-H	13.50	207.7	0.04	[5a]
1-Me	14.11	206.8	0.18	[5e]
1-OMe	13.43	187.2	2.30	[17a]
1-OMe	13.89	191.3	2.80	this work
1-OEt	13.77	188.8	3.60	this work

[a] At 300°C.

The small deviations between our data and Richey's lie well within experimental error limits, although our results are likely to possess a higher reliability. This is mainly because we have shown the absence of significant heterogeneous and radical reactions, but also because we have eliminated pressure effects and covered a wider temperature range. Variations in the values of lg$A$ and E_a for **1-OR** are, as expected, small due to only minor differences in alkoxy-donor stabilization of the postulated, ring-opened diradical intermediate **4-OR**[2,3,5i,17a].



4-OR

The ΔS^{+} values corresponding to lg$A$ in Table 7 are ca. +6 ± 5 J K^{-1} mol^{-1} for **1-OMe** and **1-OEt**. These small positive values are consistent with a rate-determining ring-opening process, **1-OR** → **4-OR**, as proposed by Frey[5i] for the **1-H** → **2-H** case (via **4-H**). The differences in ΔS^{+} (or lg$A$ in Table 7) are probably not significant because they arise from a cancellation of positive contributions (of the terminal primary C radical) and negative contributions (due to the hindered internal rotation of the resonance-stabilized allyl radical). Thus, values of ΔS^{+} close to zero are to be expected.

The slight differences in the Arrhenius parameters of **1-OR** lead to a small increase of the decomposition rate for **1-OEt** compared to **1-OMe**. Table 7 reveals a rate constant ratio, k(**1-OEt**)/k(**1-OMe**) = 1.22 at 300°C. A similar rate enhancement is also observed in the VCP-CP reactions of (*E*)-2-alkoxy-substituted vinylcyclopropanes for which k(OEt)/k(OMe) = 1.23 at 300°C[28]. These small rate enhancements, apparently transferable from one system to another, are probably ascribable to the slightly stronger electron-donating effect of OEt compared to that of OMe.

Table 8. Arrhenius parameters for *cis-trans* isomerizations of some selected 1,2-disubstituted cyclopropanes[a)]

Compound	$\lg(A/\mathrm{s}^{-1})$	E_a [kJ mol^{-1}]	Ref.
cis-1,2-dimethyl-cyclopropane	15.3	249	29)
cis-1,2-dimethoxy-*cis*-3-methylcyclopropane	14.9	209.5	30)

[a)] Despite extensive experimentation and discussion of mechanism concerning cyclopropane isomerizations (see e.g. ref.[35)]) it is still reasonably presumed that isomerization takes place mainly by fission of the bond which is disubstituted by the most activating substituents.

A point of more general interest concerns the magnitude of the radical-stabilizing effect of alkoxy groups. The lowering of activation energy by **1-OMe** in the VCP-CP rearrangement is ca. 18 kJ mol^{-1} (Table 7). This may be compared with the average difference of ca. 20 kJ mol^{-1} between methoxy- and methyl-substituent effects on a cyclopropane[29,30)] as illustrated by the data in Table 8. It would appear that the extra methoxy stabilization of an allyl-stabilized diradical such as **4-OMe** is comparable to that of methoxy stabilization of a normal radical center. This is in agreement with the results of Korth, Lommes, and Sustmann[31)] who have found very similar barriers to internal rotation in the *cis-trans* isomerization of 1-methoxy- and 1-deuterioallyl radicals (61 and 66 kJ mol^{-1}, resp.). The actual magnitude of the methoxy stabilization as obtained by bond dissociation energy (BDE) measurements may be represented by $D(\mathrm{CH_3CH_2CH_2-H}) - D(\mathrm{CH_3OCH_2-H})$. This has the magnitude of 20 kJ mol^{-1}[32)]. BDE measurements have become a topic of some controversy in recent years, and the absolute magnitudes of $D(\mathrm{R-H})$ in the alkanes are now thought to be 10 to 15 kJ mol^{-1} higher[33)] than those in the earlier review by McMillan and Golden[32)]. However, it is unlikely that substituent effects, as represented by differences, will be much affected by these changes. It would therefore appear that the methoxy-substituent effects on cyclopropane rearrangements, both with and without vinyl substituents, are highly consistent with the energetic changes expected for a diradical mechanism. Some recent theoretical calculations underestimate the stabilizing effect of the methoxy group[34)].

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Experimental

^{1}H NMR: Bruker WP 80, AW 250 (250 MHz); δ = 7.26 for $\mathrm{CHCl_3}$. – ^{13}C NMR: Bruker WH 250 (62.90 MHz); δ = 77.0 for $\mathrm{CDCl_3}$. Assignments were also made by application of the DEPT-135 method: + = primary or tertiary, – = secondary, ○ = quaternary carbons. – MS: Varian MAT CH 7 with Varian Aerograph 1740, Varian MAT 311 A (high resolution). – IR: Perkin-Elmer 297 and 399. – GC analytical: Siemens Sichromat 3 (25-m capillary column CB-SE-54, carrier gas H_2); GC preparative: Varian Aerograph 920 (carrier gas H_2; 3/8″ Teflon column with 10% SE-54 on Chromosorb W-AW-DMCS). – All reactions were performed in anhydrous solvents and under nitrogen. Starting materials have been distilled or recrystallized prior to use.

Preparation of Compounds: Starting materials and reagents ethyl 3-chloropropionate[36)], 1-ethoxy-1-(trimethylsiloxy)cyclopropane[21)], 1-ethoxy-1-cyclopropanol[22)], and trialkyloxonium tetrafluoroborates[24)] were prepared according to known literature procedures. 1-Vinyl-1-cyclopropanol (**1-OH**) was prepared according to similar procedures of Wasserman[23)]. The authentic sample of **2-OEt** was obtained by the method of Schmidt[25)], **2-OMe** similarly by an analogous method.

1-Vinyl-1-cyclopropanol (**1-OH**): To 2.43 g (100 mmol) of magnesium turnings was added dropwise 15.6 g (110 mmol) of methyl iodide. The reaction mixture was refluxed for 1 h. 10.2 g (100 mmol) 1-ethoxy-1-cyclopropanol[22)] was added to the cooled mixture (0°C). The mixture was stirred at room temp. for 1 h, then 100 ml of a 1.0 M vinylmagnesium bromide solution (100 mmol) in tetrahydrofuran (THF) was added dropwise and the resulting mixture refluxed for 15 h. After hydrolysis with 200 ml of 0.5 M $\mathrm{NH_4Cl}$ solution the organic layer was separated and the aqueous layer extracted with three portions of ether (50 ml each). The combined organic solutions were dried with $\mathrm{MgSO_4}$, ether and THF were distilled over a 20-cm Vigreux column. The residue was distilled in a microdistillation apparatus at reduced pressure to yield 5.1 g (61%) of **1-OH**, b.p. 44–46°C/17 Torr. – The spectroscopic data were consistent with those in the literature[23)].

General Procedure for Alkylations of **1-OH** *with Trialkyloxonium Tetrafluoroborates and Alkyl Trifluoromethanesulfonates:* To a stirred solution of **1-OH** in diethyl ether was added at –78°C a 1.6 M methyllithium solution in ether, after which the mixture was stirred for 30 min. Trialkyloxonium tetrafluoroborate was added in small portions (or a solution of alkyl trifluoromethanesulfonate in diethyl ether was added dropwise) and the mixture stirred at –78°C for at least 2 h. The mixture was left to warm up to room temp. and was stirred at this temperature for 16 h. According to GC analyses total conversions of **1-OH** to **1-OR** were observed in all reactions. The mixture was hydrolyzed with 5% $\mathrm{NH_4Cl}$ solution, extracted with diethyl ether and the organic layer dried with $\mathrm{MgSO_4}$. The solvent was distilled over a 50-cm packed column and the residue (containing >90% **1-OR** according to ^{1}H-NMR analyses) trap-to-trap distilled at reduced pressure. Pure ethers **1-OR** (>99.99%) could only be obtained with a substantial mass loss by repeated preparative GC separations.

1-Vinyl-1-cyclopropyl Methyl Ether (**1-OMe**)

a) According to the general procedure with 3.5 g (41.6 mmol) of **1-OH** in 30 ml of ether, 26 ml of MeLi solution (41.6 mmol), and 6.15 g (41.6 mmol) of trimethyloxonium tetrafluoroborate; yield 1.27 g (31%) **1-OMe**. – IR (film): $\tilde{\nu}$ (cm^{-1}) = 3094, 2935 (CH), 2832 ($O-CH_3$), 1640 (C=C), 1079 (C–O–C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.68 (mc, 2H, 2(3)-H), 0.99 (mc, 2H, 2(3)-H), 3.26 (s, 3H, OCH_3), 5.07 (dd, 1H, $^2J_{2'H(Z),2'H(E)} = -1.6$, $^3J_{2'H(Z),1'H}$ = 10.6 Hz, 2'-H_Z), 5.16 (dd, 1H, $^2J_{2'H(E),2'H(Z)} = -1.6$, $^3J_{2'H(E),1'H}$ = 17.2 Hz, 2'-H_E), 5.60 (dd, 1H, $^3J_{1'H,2'H(Z)}$ = 10.6, $^3J_{1'H,2'H(E)}$ = 17.2 Hz, 1'-H). – ^{13}C NMR (62.90 MHz, DEPT): δ = 14.47 [C-2(3), –], 55.11 (OCH_3, +), 62.54 (C-1, ○), 112.12 (C-2', –), 138.64 (C-1', +). – MS (70 eV): *m/z* (%) = 98 (14) [M^+], 97 (100) [M – 1], 83 (5) [M – Me], 71 (3) [M – C_2H_3], 67 (46) [M – OMe], 55 (40), 53 (10).

b) According to the general procedure with 0.5 g (5.94 mmol) of **1-OH** in 10 ml of ether, 3.7 ml of MeLi solution (5.94 mmol), and 0.97 g (5.94 mmol) of methyl trifluoromethanesulfonate in 5 ml of ether; yield 0.17 g (29%) of **1-OMe**. – For spectroscopic data see under a).

1-Vinyl-1-cyclopropyl Ethyl Ether (**1-OEt**)

a) According to the general procedure with 3.0 g (35.7 mmol) of **1-OH** in 50 ml of ether, 22.3 ml of MeLi solution (35.7 mmol), and 6.78 g (35.7 mmol) of triethyloxonium tetrafluoroborate; yield 1.6 g (40%) of **1-OEt**. – IR (film): $\tilde{\nu}$ (cm^{-1}) = 3092, 2977 (CH), 1641 (C=C), 1068 (C–O–C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.68 [mc, 2H, 2(3)-H], 1.00 [mc, 2H, 2(3)-H], 1.16 (t, 3H, OCH_2CH_3), 3.51 (q, 2H, OCH_2CH_3), 5.04 (dd, 1H, $^2J_{2'H(Z),2'H(E)} = -1.6$, $^3J_{2'H(Z),1'H}$ = 10.8 Hz, 2'-H_Z), 5.14 (dd, 1H, $^2J_{2'H(E),2'H(Z)} = -1.6$, $^3J_{2'H(E),1'H}$ = 17.4 Hz, 2'-H_E), 5.62 (dd, 1H, $^3J_{1'H,2'H(Z)}$ = 10.8, $^3J_{1'H,2'H(E)}$ = 17.4 Hz, 1'-H). – ^{13}C NMR (62.90 MHz, DEPT): δ = 14.50 [C-2(3), –], 15.46 (OCH_2CH_3, +), 61.48 (C-1, ○), 62.95 (OCH_2CH_3, –), 111.67 (C-2', –), 139.38 (C-1', +). – MS (70 eV): *m/z* (%) = 112 (2) [M^+], 111 (13) [M – 1], 85 (4) [M – C_2H_3], 84 (72), 83 (100) [M – Et], 67 (21), [M – OEt], 57 (16), 56 (21), 55 (98).

$C_7H_{12}O$ Calcd. 112.0888 Found 112.0867 (MS)

b) According to the general procedure as above with 0.8 g (9.51 mmol) of **1-OH** in 15 ml of ether, 5.9 ml of MeLi solution (9.51 mmol), and 1.69 g (9.51 mmol) of ethyl trifluoromethanesulfonate in 10 ml of ether; yield 0.38 g (36%) of **1-OEt**. – For spectroscopic data see under a).

Kinetic Measurements: These were performed in an apparatus similar to that used in previous studies. This also applies to the experimental procedure for collecting the kinetic data[26a-d]. It should be emphasized that before *every* pyrolytic run was performed, a blank sample of the master mixture was analyzed by GC in order to check for constant composition and provide a reference for mass recovery checks in kinetic runs. As the master mixture compositions proved to be stable, average composition values for substances were used in calculations (see e.g. Table 3).

Analysis: All quantitative analyses were performed on a Perkin-Elmer 8310 Gas Chromatograph with a GP-100 Graphics Printer. Separations were carried out on a 7-m × 3-mm silicon oil column (15% MS 550 on 60/80 Chromosorb P) with which excellent separations for all substances were achieved. Column temperatures were 80°C for studies of **1-OMe** and 90°C for studies of **1-OEt**. Separations were performed at constant carrier gas (N_2, 123 kPa), hydrogen (133 kPa), and air (81 kPa) pressures. Under these conditions the following reproducible retention times were recorded: 80°C: propene, 1.80 min; cyclohexane (CH), 6.10 min; **1-OMe**, 8.53 min; **2-OMe**, 16.26 min. 90°C: **3**, 1.70 min; *cis*-2-butene, 2.14 min; CH, 5.15 min; **1-OEt**, 9.01 min; **2-OEt**, 19.56 min. Product identities were exclusively confirmed by a retention time comparison with authentic samples (**2-OMe**, **2-OEt**, **3**). Isomeric compounds and the CH standard were assumed to have the same FID response factors. For **3**, a correction of the FID response factor by a realistic multiplication factor of 3.5 was necessary.

CAS Registry Numbers

1-OMe: 49785-10-6 / **1-OEt**: 130933-90-3 / **1-OH**: 22935-31-5 / **2-OMe**: 1072-59-9 / **2-OEt**: 17065-24-6 / 1-ethoxy-1-cyclopropanol: 13837-45-1 / vinyl bromide: 593-60-2

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