Thermal rearrangement of methyl *cis*-2-alkylcyclopropanecarboxylates[1]

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Seven alkyl substituted methyl cyclopropanecarboxylates with an alkyl group *cis* to the ester group have been found to ring open to the isomeric γ,δ-unsaturated ester through a 1,5-hydrogen shift upon heating to 259.4 °C in a sealed tube. Methyl cyclopropanecarboxylates which do not have a *cis* 2-alkyl group are unaffected when heated for longer periods at this or higher temperatures and thus a simple method for determining geometrical isomers in this series is now available. The reactions are first-order, with $\Delta H\dagger$ between 25 and 38 kcal/mole and $\Delta S\dagger$ between −8 and −37 e.u. This and other information fully supports a cyclic hydrogen transfer mechanism.

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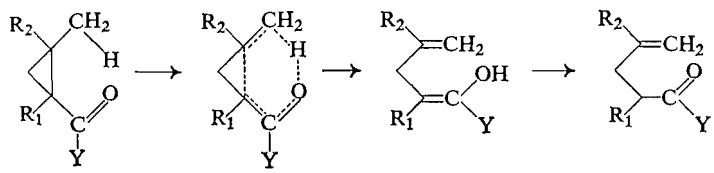


1 **2** **3** **4**

In an earlier communication (1) we described a thermal rearrangement of methyl *cis*-2-alkylcyclopropanecarboxylates[2] which did not take place for the isomeric *trans* esters. A number of other systems which are directly related to the ester rearrangement can be represented by the reaction **1** → **4**. Anhydrides (2), ketones (3–6), aldehydes (7), vinyl cyclopropanes (8), *N*-acylaziridines (9), and possibly phenylcyclopropanes (10) are known to react in this manner. The most extensive mechanistic study to date has been on a series of ketones (4) and from this work enolene intermediates (**3**) are strongly indicated. Kinetic studies on the vinylcyclopropanes (8) and ketones (4) show good first-order plots and suggest a highly organized intermediate (large negative entropy) compatible with the description shown in **2**. The fact that hydrogen migration occurs only when the carbonyl or vinyl group is *cis* to an alkyl group on the vicinal ring carbon has been noted in several studies (3–8).

In the present study we have determined the kinetics for the rearrangement of several alkyl substituted methyl cyclopropanecarboxylates. From the data presented we are able to standardize the conditions of the reaction so that *cis* and *trans* stereochemical evaluations can be made with only one isomer at hand and we have been able to verify the mechanism proposed earlier.

The compounds studied and the products isolated from the rearrangement are shown in Table I. Most of the starting materials were available from earlier work in this laboratory and the others were prepared by standard methods as described in the Experimental. The products were all isolated in a pure state by vapor-phase chromatography and identified as described in the Experimental. These reactions yielded γ,δ-unsaturated esters free of any by-products and as such are an excellent synthetic method. In the case where the alkyl group vicinal to the ester is an ethyl group two products were formed (*cis*- and *trans*- γ,δ-unsaturated esters) depending on which of the hydrogens migrates. These could be readily distinguished due to the fact that the *trans* isomer gave the characteristic infrared band at 970 cm^{-1} for the *trans vicinal* hydrogens on a carbon double bond.

[1]Taken in part from the Ph.D. Thesis of N. W. K. Chiu, September, 1967.

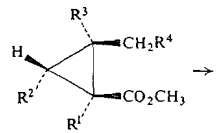
[2]Throughout this paper *cis* will refer to the structure having the alkyl group on C-2 *cis* to the carbomethoxy group.

TABLE I

Parameters for the thermal rearrangement of a number of methyl cyclopropanecarboxylates[a]

Methyl 1-cyclopropanecarboxylates		R^1	R^2	R^3	R^4	Methyl 4-pentenoate (**18**)	$t_{1/2}$[b] (259.4°) (h)	$\Delta H\dagger$ (kcal/mole)	$\Delta S\dagger$ (e.u.)
1,2,2-Trimethyl (**5**)		CH_3	H	CH_3	H	2,4-Dimethyl (**12**)	2.26	37.5	−8
1-Methyl-2-ethyl (**6**)	(11)	CH_3	H	H	CH_3	Methyl *cis*- and *trans*-2-methyl-4-hexenoate (**13** and **14**)	12.62	33.9	−18
2,2-Dimethyl (**7**)		H	H	CH_3	H	4-Methyl (**15**)	15.16	36.1	−14
1,2-Dimethyl (**8**)	(12)	CH_3	H	H	H	2-Methyl (**16**)	16.30	30.2	−25
2,3-Dimethyl (**9**)	(12)	H	CH_3	H	H	3-Methyl (**17**)	28.46	32.5	−22
2-Methyl (**10**)	(13)	H	H	H	H	(**18**)	31.39	35.9	−17
1,2,3-Trimethyl (**11**)	(14)	CH_3	CH_3	H	H	2,3-Dimethyl (**19**)	45.00	25.2	−37

[a]The structural configuration can be represented by:



$\rightarrow R^4CH{=}CR^3CHR^2CHR^1CO_2CH_3$.

[b]Maximum error is estimated to be ±5% for k corresponding to ±2 kcal/mole for $\Delta H\dagger$ and ±4 e.u. for $\Delta S\dagger$.

Mechanism

First-order plots of the kinetics, determined on samples in sealed tubes where each point is a different sample and where the composition of the reaction mixture was determined by vapor-phase chromatography, gave good straight lines as illustrated in Fig. 1. The low degree of scatter of the points and the fact that the plots pass through the origin fully support the first-order kinetics observed and exclude a free radical chain process.

The half-lives at 259.4 °C, the heat of activation, and the entropy of activation were calculated and are listed in Table I.

As a further test of the mechanism the *trans* isomers corresponding to structures **6**, **8**, **9**, and **10** and the isomeric nitriles *cis*- and *trans*-1,2-dimethyl-1-cyanocyclopropane were heated for prolonged periods at 258 °C or higher and in all cases no evidence for rearrangement could be found.

The values of $\Delta H\dagger$ and $\Delta S\dagger$ are in line with the thermodynamic parameters reported for *cis*-2-methyl-1-vinylcyclopropane (8, $E_a = 31$ kcal/mole and $\Delta S\dagger = -11.6$ e.u.) and 1-acetyl-2,2-dimethylcyclopropane (4, $\Delta H\dagger = 30$ kcal/mole, $\Delta S\dagger = -10$ e.u.). The large negative entropy of activation in all examples fully supports an ordered transition state as illustrated by structure **2**. The high stability of the *trans* isomers of **6**, **8**, **9**, and **10** and of the nitriles also supports this transition state, for in these compounds the multiple bonds are no longer in the proximity of the alkyl group from which a hydrogen must migrate. Clearly this proximity is a necessary requirement.

It is therefore possible to discuss the reaction in light of this mechanism. The 2-ethyl derivative (**6**) gave two γ,δ-derivatives. Examination of Dreiding models of the transition states expected for migration of each of the methylene hydrogens shows that one (the one that would give the *cis* double bond in the product) has a major steric interaction between the methyl of the ethyl group and the ring carbons. This or an equivalent steric factor is not present for the transition state that leads to the *trans* product. The ratio of *trans*:*cis* in the product of 4.7:1 can therefore be rationalized.

We can now compare the rate of formation of the *trans* product ($t_{1/2}$ at 259.4 °C is 15.3 h) from **6** with that for the formation of **16** from **8** with corrections for the statistically faster rate due to the three available hydrogens ($t_{1/2}$ at 259.4 °C is 48.9 h per hydrogen). A faster rate of reaction is obtained for migration of a secondary hydrogen over that of a primary hydrogen as would be expected if bond breaking of the C—H bond were important in the transition state as proposed by Frey (8) and illustrated by intermediate **2**.

The alkyl substituted cyclopropanecarboxylates studied give a 20-fold variation in rate at 259.4 °C. Factors which influence this variation may be steric or electronic. It is significant that in the series **10**, **9**, **8**, **6**, and **5** increasing substitution on C-1 and C-2 increases the rate. Substitution on C-1 to C-2 would be expected to weaken that bond and thus the breaking of the C-1 and C-2 bond must also be an important feature of the transition state as indicated by structure **2**.

The presence of a substituent on C-3 as in **11** where it is *cis* to the methyl at C-1 clearly creates a steric factor in the transition state which is unfavorable. This would suggest that for the transition state from **11** the *cis* methyls are closer to being fully eclipsed, than in **11**, contributing to a slower rate and larger negative entropy. As a corollary we might therefore suggest, that for cyclopropanes in general, the presence of bulky groups can cause the structure to twist away from a fully eclipsed conformation.

Finally it should be noted that when the unsaturated group in **1** is a ketone the reaction is faster (compare 1-acetyl-2,2-dimethylcyclopropane with $t_{1/2}$ of 4.8 h at 152 °C (4) with compound **7**). This order suggests ionic character in the reaction, related to the greater nucleophilic nature of a ketone oxygen than the oxygen of an ester carbonyl. The facile rearrangement of methyl 2,2-dimethyl-1-cyanocyclopropanecarboxylate (1) and 2-methyl-1,1-diacetylcyclopropane (5) may also reflect easier bond breaking of the C-1 to C-2 bond in an ionic sense which fits an alternating pattern of −,+,−,+,−,+ for the 6 atoms in the transition state, beginning at the oxygen.

Conclusions

In conclusion we can state that the cyclic unimolecular mechanism is fully supported for the series of *cis*-2-alkyl-1-cyclopropanecarboxylates described herein. The lack of reaction for

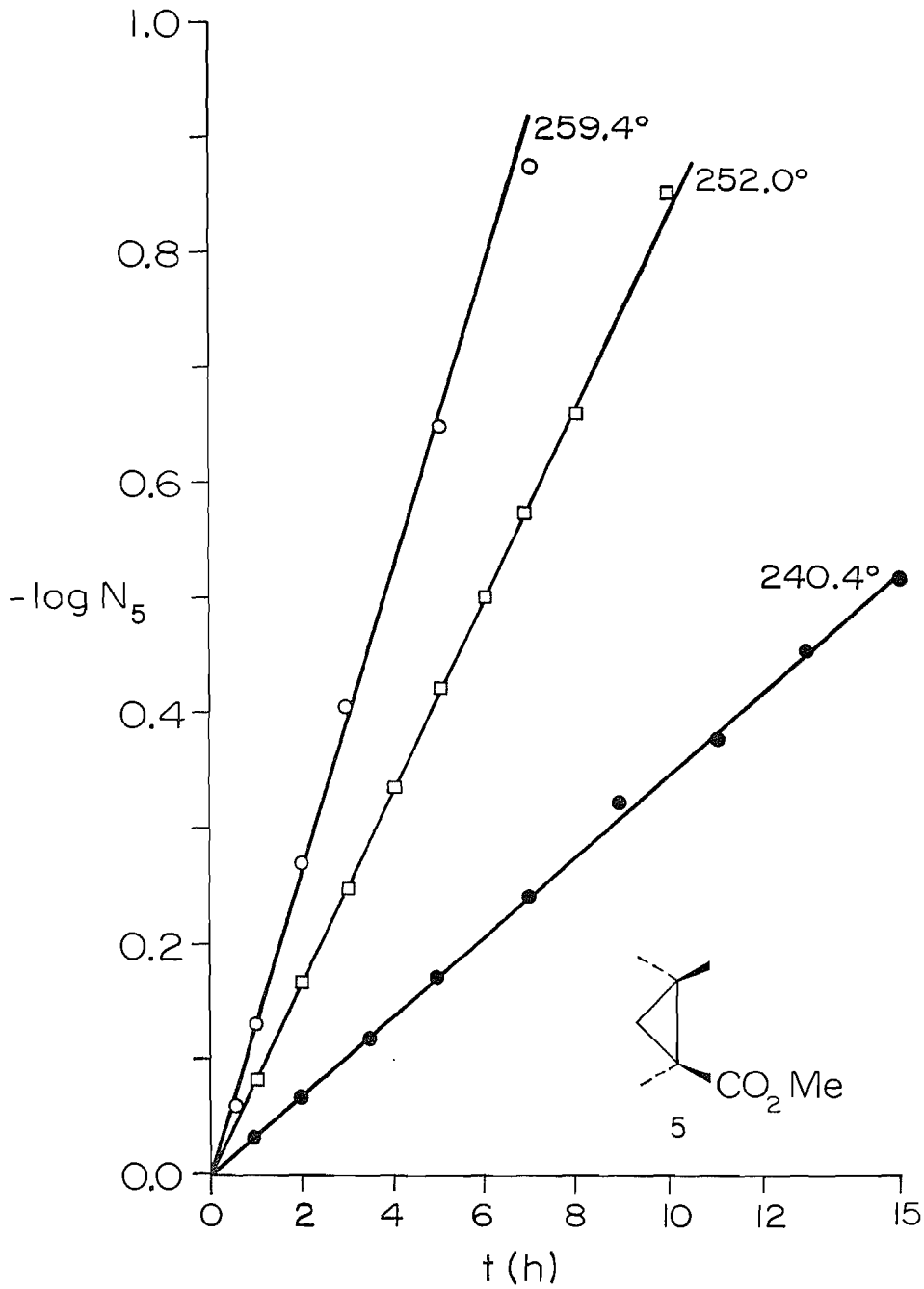


FIG. 1. First-order rate plots for the thermal isomerization of **5**.

the corresponding *trans* isomers under more vigorous reaction conditions clearly makes this reaction useful for determining the stereochemistry directly when only a single isomer is at hand. Indeed we have based the structural assignments for **6** (11), **8** (1), and **11** (14) and their *trans* isomers on this reaction. Similarly *cis*-1,2-dimethyl-1-acetylcyclopropane has been distinguished from the *trans* isomer (6).

The most useful method to date for determining geometry of cyclopropane derivatives has been based on the cyclic anhydride formation possible only from a *cis*-1,2-dicarboxylic acid (15). This reaction has been applied in some extensive studies recently (16). Cyclopropanecarboxylic acids with a hydrogen on the α-carbon can be equilibrated in base or thionyl chloride to give the more stable configuration (17, 18). Steric factors also influence the rate of hydrolysis of cyclopropanecarboxylate esters and this has been used to distinguish **8** from its *trans* isomer (19). The use of nuclear magnetic resonance (n.m.r.) is promising as the coupling constants for vicinal ring hydrogens are greater for the *cis* orientation (8–11 Hz) than for the *trans* (5–8 Hz) (see refs. 20–22 for further discussion). Although n.m.r. has been used (14, 17) successfully it is frequently limited by the complexity of the spectra which often have overlapping signals. We anticipate therefore that our new method of assigning stereochemical configuration will be most useful.

Experimental

Boiling points recorded are not corrected and were determined by the micro-inverted capillary method. Infrared spectra were recorded on a Perkin–Elmer model 21DB spectrophotometer and were calibrated using the 1603 cm^{-1} band of a polyethylene film. The nuclear magnetic resonance (n.m.r.) spectra were determined on 20% by volume solutions in carbon tetrachloride using a Varian A-60 and/or a Varian HA-100 spectrometer. All samples were separated by a Varian aerograph model A-90-P chromatograph and integrations of the peak areas were achieved using a disk integrator fitted to a Honeywell electronic 15 recorder.

Compounds prepared or identified elsewhere are described in the references cited in Table I. The following procedures were used to prepare the remaining cyclopropanes.

Methyl 1,2,2-Trimethyl-1-cyclopropanecarboxylate (5)

The 3,5,5-trimethyl-3-carbomethoxy-1-pyrazoline used to prepare **5** was obtained from the reaction of 2-diazopropane (23) with methyl methacrylate. A mixture of 58 g (0.25 mole) of silver oxide, 25 g (0.25 mole) of methyl methacrylate, and 300 ml of anhydrous ether was cooled to −60 °C. While the reaction medium was stirred 18 g (0.25 mole) of acetone hydrazone were added over a 10 min period. The mixture was stirred at −25 °C for 1 h and then slowly warmed to room temperature. The residual solids were filtered off and the filtrate evaporated and distilled to give 15 g of the pyrazoline, b.p. 55–56 °C at 0.1 mm.

Anal. Calcd. for $C_8H_{14}O_2N$: C, 56.47; H, 8.23; N, 16.47. Found: C, 56.30; H, 8.13; N, 16.35.

The n.m.r. spectrum confirmed the structure showing peaks at τ 6.27 (ester methyl), τ 8.03 and τ 8.79 (doublets with J_{gem} = 13.1 Hz for the AB system of the hydrogens on C-4) and τ 8.46, τ 8.60, and τ 8.64 (ring methyls on C-3 and C-5). Pyrolysis of 12.5 g of 3,5,5-trimethyl-3-carbomethoxy-1-pyrazoline at 90–100 °C gave 9.5 g of product which when analyzed by v.p.c. using a dinonyl phthalate column at 158 °C gave two products:

(*i*) Methyl 1,2,2-trimethyl-1-cyclopropanecarboxylate (**5**), 85%, b.p. 148.5 °C, n_D^{25} 1.4280 with n.m.r. (20% in benzene) peaks at τ 6.57 (ester methyl), τ 8.74, τ 8.87, and τ 9.01 (ring methyls) and τ 8.58 and τ 9.74 (doublets with J_{gem} = 4.6 Hz for the AB system of the hydrogens on C-3).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.69; H, 9.88.

(*ii*) Methyl *trans*-2,4-dimethyl-2-pentenoate, 15%, b.p. 164.5 °C, n_D^{25} 1.4366 (lit. (24), b.p. 49–50 °C at 10 mm, n_D^{20} 1.4383). The *trans* geometry is based on comparison with the *cis* isomer available by an independant synthesis (25).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.85; H, 9.71.

Methyl 2,2-Dimethyl-1-cyclopropanecarboxylate (7)

The 5,5-dimethyl-3-carbomethoxy-1- and 2-pyrazoline used to prepare **7** were obtained from the reaction of 2-diazopropane with methyl acrylate. The crude pyrazoline which was clearly a mixture of the 1- and 2-pyrazolines as indicated by n.m.r. was not further purified but was pyrolyzed directly to give a pyrolysis mixture which was separated on a dinonyl phthalate column at 165 °C to give two components.

Methyl 2,2-dimethyl-1-cyclopropanecarboxylate (**7**), 26%, was the major compound in the more volatile component. However methyl *cis*-4-methyl-2-pentenoate, 4%, was also present and could not be removed. This component however did not interfere with the identification of **7** nor the kinetics on **7**.

Anal. Calcd. for the mixture $C_7H_{12}O_2$: C, 65.49; H, 9.45. Found: C, 65.37; H, 9.62.

The n.m.r. spectrum of **7** showed peaks at τ 6.37 (ester methyl), τ 8.81, and τ 8.86 (ring methyls), τ 8.50, τ 9.21, and about τ 8.95 (ring hydrogens on C-1, C-2 *cis*, and C-2 *trans* showing J_{gem} = 4.0 Hz, J_{cis} = 8.1 Hz, and J_{vic} = 5.1 Hz) in accord with that of the corresponding acid (22).

Methyl *trans*-4-methyl-2-pentenoate, 70%, b.p. 150 °C, n_D^{22} 1.4298 had the expected n.m.r. spectrum (25) in addition to the infrared band at 990 cm^{-1} characteristic of a *trans* H—C=C—H unit.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.49; H, 9.45. Found: C, 65.39; H, 9.44.

cis- and trans-1,2-Dimethyl-1-cyanocyclopropane

Addition of a solution of diazoethane in ether to methacrylonitrile gave on evaporation of the solvent a

mixture of *cis*- and *trans*-3,5-dimethyl-3-cyano-1-pyrazoline. Pyrolysis of 10 g of this pyrazoline mixture at 100 °C gave a product which showed three components when analyzed on a dinonyl phthalate column at 145 °C. The components were assigned structures by comparison of the physical data with those found for the corresponding esters isolated from an analogous reaction (14).

trans-1,2-Dimethyl-1-cyanocyclopropane, 53%, b.p. 137.5 °C, n_D^{26} 1.4179 showed no n.m.r. signals below τ 8.65.

Anal. Calcd. for C_6H_9N: C, 75.74; H, 9.54; N, 14.72. Found: C, 75.82; H, 9.67; N, 14.92.

cis-1,2-Dimethyl-1-cyanocyclopropane, 44%, b.p. 149 °C, n_D^{26} 1.4238 showed no n.m.r. signals below τ 8.50.

Anal. Calcd. for C_6H_9N: C, 75.74; H, 9.54; N, 14.72. Found: C, 75.72; H, 9.80; N, 14.82.

γ,δ-Unsaturated Esters

Samples of the cyclopropane esters **5** to **11** were heated at 280 °C until n.m.r. or v.p.c. showed rearrangement to be nearly complete. Separation by v.p.c. from any remaining starting material gave the pure γ,δ-unsaturated ester.

Methyl 2,4-dimethyl-4-pentenoate (**12**), b.p. 155 °C, n_D^{24} 1.4228 (lit. (26), b.p. 51 °C at 12 mm, n_D^{20} 1.4270) from **5** was separated on a didecyl phthalate column at 150 °C to give a relative retention time of 1.13 with respect to **5**.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.42; H, 10.14.

The n.m.r. spectrum was consistent with this assignment showing peaks at τ 5.31 (terminal olefinic hydrogens), τ 6.41 (ester methyl), τ 7.20–8.10 (multiplet for hydrogens on C-2 and C-3), τ 8.31 (methyl on C-4), τ 8.91 (doublet for the methyl on C-2 with $J = 6.5$ Hz).

Methyl *cis*-2-methyl-4-hexenoate (**13**), b.p. 164.5 °C, n_D^{26} 1.4261, 17.5% from **6** was separated on a diethylene glycol succinate column at 153 °C and gave a relative retention time of 1.41 with respect to the *trans* isomer (**14**).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.33; H, 9.97.

The n.m.r. spectrum showed peaks at τ 4.25 to τ 4.95 (multiplet for the olefinic hydrogens), τ 6.40 (ester methyl), τ 7.35 to τ 8.05 (multiplet for the hydrogens on C-2 and C-3), τ 8.39 (doublet for the hydrogens on C-6 with $J = 5.7$ Hz) and τ 8.88 (doublet for the methyl on C-2 with $J = 6.3$ Hz).

Methyl *trans*-2-methyl-4-hexenoate (**14**), b.p. 161 °C, n_D^{26} 1.4225, 82.5% from **6**, was distinguished from the *cis* isomer **13** by the presence in its infrared spectrum of a band at 973 cm^{-1} characteristic of *trans* vicinal disubstituted olefins.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.36; H, 10.00.

The n.m.r. spectrum showed peaks at τ 4.50 to τ 5.00 (multiplet for the olefinic hydrogens), τ 6.41 (ester methyl), τ 7.50 to τ 8.10 (multiplets for the hydrogens on C-2 and C-3), τ 8.36 (doublets for the hydrogens on C-6 with $J = 4.7$ Hz) and τ 8.96 (doublet for the methyl on C-2 with $J = 6.5$ Hz).

The final ratio of *trans*:*cis* of 4.7:1 corresponded well with the ratio observed after partial reaction during kinetic runs where values of 4.5, 5.0, 5.2, 4.8, 4.0, and 5.3 were observed. Heating of **13** and **14** at 296 °C for 20 h gave only about 5% conversion of each isomer into the other. It is interesting to note that this *cis* ⇄ *trans* isomerization is not accompanied by any double bond migration (25).

Methyl 4-methyl-4-pentenoate (**15**), b.p. 149 °C, n_D^{23} 1.4230 was prepared from **7**. This experiment was complicated by the fact that **7** contained 15% of methyl *cis* 4-methyl-2-pentenoate which under the reaction conditions isomerized to methyl 4-methyl-3-pentenoate (25). On a dinonyl phthalate column at 155 °C the starting material **7**, the product **15** and the 3-pentenoate had retention times of 14.7, 18.9, and 23.3 respectively.

Anal. Calcd. for **15**, $C_7H_{12}O_2$: C, 65.49; H, 9.45. Found: C, 65.67; H, 9.53.

The n.m.r. spectrum of **15** showed peaks at τ 5.20 (broad singlet for the terminal olefinic hydrogens), τ 6.35 (ester methyl), τ 7.64 (singlet for the hydrogens on C-2 and C-3), and τ 8.25 (broad singlet for the methyl on C-4).

Methyl 2-methyl-4-pentenoate (**16**), b.p. 137.5 °C, n_D^{22} 1.4156 from **8** was isolated using a dinonyl phthalate column at 140 °C.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.49; H, 9.45. Found: C, 65.68; H, 9.57.

The n.m.r. spectrum showed peaks at τ 4.15 to τ 4.85 (multiplet for the C-4 olefinic hydrogen), τ 5.05 and τ 5.26 (broadened multiplets for the terminal olefinic hydrogens), τ 6.49 (ester methyl), τ 7.35 to τ 8.10 (multiplet for the hydrogens on C-2 and C-3), and τ 8.97 (doublet for the methyl on C-2 with $J = 6.5$ Hz).

Methyl 3-methyl-4-pentenoate (**17**), b.p. 137.5 °C, n_D^{24} 1.4152 from **9** was isolated using a dinonyl phthalate column at 150 °C.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.49; H, 9.45. Found: C, 65.58; H, 9.45.

The n.m.r. spectrum showed peaks at τ 4.22, τ 4.95, and τ 5.18 (broad multiplets for the olefinic hydrogens), τ 6.41 (ester methyl), τ 7.35 (multiplet for the hydrogen on C-3), τ 7.76 and τ 7.76 (overlapping doublets for the nonequivalent methylene at C-2 with $J = 8.6$ and 5.8 Hz respectively), and τ 8.97 (doublet for the methyl on C-3 with $J = 5.3$ Hz).

Methyl 4-pentenoate (**18**), b.p. 125.5 °C, n_D^{22} 1.4148 was obtained from a mixture of **10** and its *trans* isomer, determined by the OCH_3 peak of the n.m.r. at 100 MHz to be in the proportions 28:72 respectively (the OCH_3 of the *cis* ester appears at lower field). Attempts to separate these isomers have been unsuccessful except on capillary columns. The methyl 4-pentenoate was separated from the methyl *trans*-2-methylcyclopropanecarboxylate on a Ucon polar column at 92 °C and had a relative retention time of 0.85 and gave the following analysis.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.11; H, 8.84. Found: C, 62.90; H, 8.81.

The n.m.r. spectrum showed peaks at τ 4.09, τ 4.84, and τ 5.08 (multiplets for the olefinic hydrogens), τ 6.45 (ester methyl) and τ 7.62 and τ 7.67 (singlets for the hydrogens on C-2 and C-3).

Methyl 2,3-dimethyl-4-pentenoate (**19**), b.p. 151.5 °C, n_D^{23} 1.4212 was obtained by heating a mixture of methyl *cis,trans*-1,2,3-trimethylcyclopropanecarboxylate and its isomer with the methyls all *cis* (14). Separation on a didecyl phthalate column at 168 °C gave pure **19** with a relative retention time of 0.93 with respect to the unchanged isomer with all methyls *cis*.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.71; H, 9.91.

The n.m.r. spectrum of **19** showed peaks at τ 4.31, τ 4.92 and τ 5.14 (multiplets for the olefinic hydrogens), τ 6.38 (ester methyl), τ 7.64 (multiplets for the hydrogens on C-2 and C-3), τ 8.94 and τ 9.01 (doublets for the methyls on C-2 and C-3 with J = 6.7 and 6.6 Hz respectively).

Kinetics

Cyclopropane samples for the kinetic runs were estimated to be better than 99.9% pure by v.p.c. except in the case of **10** which was mixed with methyl *trans*-2-methylcyclopropanecarboxylate (*cis*:*trans* ratio of 28:72). For each run 10–15 samples of about 7 μl each were sealed in pyrex tubes 4 × 120 mm in size (approximate volume 500 μl) at atmospheric pressure and placed in a vertical cylindrical induction furnace. At appropriate time intervals samples were removed and quenched in ice–water and analyzed by vapor chromatography. The disk integrator method of analysis yielded less than ±1% error for known samples in a ratio of 1:1 and 1:2 and thus corrections for thermal conductivity differences between samples were not made. The furnace temperature was controlled to ±0.5 °C by means of Temcometer input controller. The thermometer used to record the temperature, which was placed level with the samples in the furnace, had 1 ° subdivisions and was calibrated in the range 240 to 340 °C against a N.B.S. calibrated thermometer. No corrections were made for thermal variations within this static system.

First-order plots of all kinetic data taken to over 70% completion gave good straight lines as illustrated in Fig. 1.

TABLE II

First-order rate constants[a]

Compound	Rate constant ($s^{-1} \times 10^5$)	Temperature (°C)
5	2.21	240.4
	5.35	252.0
	8.53	259.4
6	1.53	259.4
	3.25	272.2
	6.50	283.7
7	1.27	259.4
	2.95	272.2
	5.92	283.7
8	1.18	259.4
	2.41	272.2
	4.31	283.7
9	0.68	259.4
	1.37	272.2
	2.68	283.7
	5.46	297.4
10	0.61	259.4
	1.45	272.2
	2.98	283.7
	6.29	294.4
11	0.43	259.4
	0.85	272.2
	1.35	283.7
	1.26	283.7
	2.23	297.4

[a]Values used for calculation of $\Delta H\dagger$ and $\Delta S\dagger$.

The first-order rate constant at various temperatures used for calculation of $\Delta H\dagger$ and $\Delta S\dagger$ are listed in Table II.

The major factor contributing to errors is believed to be in the control of the temperature which with a ±0.5 ° range can amount to as much as ±5% error in the rates. The low degree of scatter in the plots suggests that other errors are minimal.

Acknowledgments

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