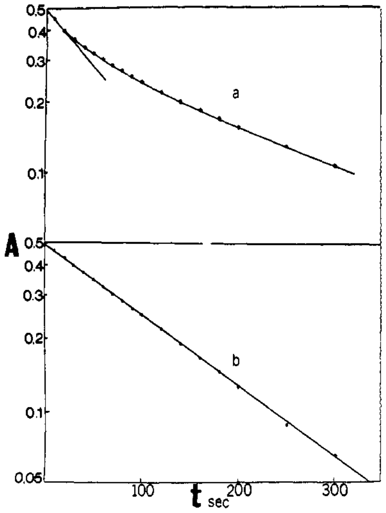

Figure 1. Plot of the reaction of 0.462 M 2-methylbenzophenone with 0.124 M methylmagnesium bromide: (a) with no added magnesium bromide; (b) in the presence of 0.0480 M magnesium bromide demonstrating the first-order behavior of the species CH_3MgBr.

and ketone do not absorb at 410 mμ, the equilibrium constant K_3 could not be evaluated in the media of high ketone concentration, but could be evaluated from spectral data at 305 mμ using 0.00088 M ketone and 0.0232–0.116 M magnesium bromide. The value of the rate constant k_2 was taken from our earlier work with dimethylmagnesium.[2] Variations in the zero time absorbancy caused by addition of $MgBr_2$ indicated a value of 0.0022 for the Schlenk constant K_s.

Using the values for the constants as stated above, k_1, the bimolecular rate constant for the reaction of CH_3MgBr with 2-methylbenzophenone,[3] was computed. A consistent value for k_1 should arise in separate experiments if the model properly describes the system and if all the constants employed are accurate. The results shown in Table I give a surprisingly consistent value for k_1 in experiments in which the ketone concentration is varied.

Table I. Rate Constants, k_1, Calculated for the Reaction of CH_3MgBr with 2-Methylbenzophenone[a]

$[K]_0$	Initial k_{obsd}, sec^{-1}	k_1, l. mol^{-1} sec^{-1}
0.128	0.00445	0.0284
0.230	0.00685	0.0253
0.343	0.00879	0.0215
0.448	0.0108	0.0213
0.563	0.0138	0.0245
0.668	0.0149	0.0222
0.892	0.0217	0.0314
1.10	0.0262	0.0349
	Av	0.0261 ± 0.004

[a] $[G]_0 = 0.0124\ M$, $K_s = 0.0022$.

If this model is correct, it should be possible to obtain more directly an experimental value for k_1 by adding additional magnesium bromide to the reaction mixture, thus driving the Schlenk equilibrium far enough to the left so that the amount of dimethylmagnesium is insignificant. As magnesium bromide is increased in amount in a set of experiments at a constant excess of ketone, two effects are observed: (1) the observed initial rate constants decrease to a certain value, then remain constant regardless of the excess of magnesium bromide employed, and (2) the first-order plots become linear. The results of such a set of experiments are shown in Table II, and two individual experiments are shown in Figure 1.

Table II. Reaction of 0.124 M Methylmagnesium Bromide with 0.462 M 2-Methylbenzophenone in the Presence of Added Magnesium Bromide

$[MgBr_2]$	Initial k_{obsd}, sec^{-1}	Ratio of $MgBr_2$:Grignard	k_1,[c] l. mol^{-1} sec^{-1}
0.0480	0.00680[a]	4:1	0.0251
0.0250	0.00672[a]	2:1	0.0243
0.0120	0.00672[b]	1:1	0.0239
0.00623	0.00693		
0.00268	0.00872	Av	0.0244 ± 0.0004
0.00156	0.00930		
0.000	0.0105		

[a] First-order plot linear for >80% reaction. [b] First-order plot linear for 30% reaction. [c] Calculated by use of the equation $k_1 = k_{obsd}(1 + K_1[K])/[K]$ where [K] is a corrected value which takes into account the ketone which is complexed by $MgBr_2$.

The absolute amount of free ketyl formed in the reaction is apparently very small since product studies under the actual conditions of the kinetics gave 100% yield of addition product. In addition, uv analysis shows that the rate of formation of the ketyl is much slower than the rate of alkylation. These conclusions apply strictly to the system studied.

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(2) J. Laemmle, E. C. Ashby, and H. M. Neumann, *J. Amer. Chem. Soc.*, in press.

(3) This does not imply that the reaction of CH_3MgBr with ketone occurs exclusively by bimolecular collision as this cannot be determined by kinetics. It is convenient for computational purposes to use the bimolecular constant. If reaction occurs by rearrangement of the complex, then the unimolecular constant $k_u = k_1K_1$.

2,3,4,4-Tetramethyloxetene. Kinetics of Rearrangement Compared to Cyclobutene–Butadiene Conversions

Sir:

Molecules in which a methylene group is replaced by an oxygen atom sometimes possess properties very different from those of their all-carbon analogs. Some examples are α-pyranes[1] which, contrary to cyclohexadienes, exhibit photo- and thermochromic behavior in certain compounds, oxirenes[2] which are orders of magnitude less stable to unimolecular rearrangement than cyclopropenes, and dioxetanes[3] which fragment with the production of light, whereas cyclobutanes fragment with much larger activation energies without luminescence.

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(1) J. B. Flannery, Jr., *J. Amer. Chem. Soc.*, **90**, 5660 (1968), and examples cited therein.

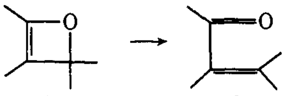
(2) G. Frater and O. P. Strausz, *ibid.*, **92**, 6654 (1970).

(3) (a) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); (b) E. H. White, J. Wiecko, and D. R. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969); (c) P. D. Bartlett and A. P. Schaap, *ibid.*, **92**, 3223 (1970); (d) S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970).

In part, the differential behavior of many oxygenated heterocyclic compounds compared to all-carbon cases is because destabilization of the oxygen-containing starting material lowers the energy of activation for certain reactions. For example, dioxetanes are destabilized by electron–electron repulsion between the nonbonded electrons of the oxygen atoms and fragment much faster than cyclobutanes. Similarly, oxirenes are predicted to be very unstable because of the 4π electron system in the starting material.

Another related feature, however, which affects the energy of the rate-determining transition state in all concerted and some stepwise reactions is the stability of the rearranged product. In general, fragmentations of heterocyclic compounds containing oxygen, which convert the hybridization of oxygen from sp^3 to sp^2, are more exothermic than fragmentations of all-carbon analogs. Using Franklin group equivalents,[4] a ketonic carbonyl group is *ca.* 5 kcal/mol lower in energy than the sum of unstrained tetrahedral carbon and oxygen atoms, whereas a trisubstituted olefinic double bond is *ca.* 20 kcal/mol higher in energy than the two respective tetrahedral carbon atoms. If the transition state of a fragmentation is sufficiently advanced along a reaction coordinate that converts a tetrahedral oxygen atom to a trigonal carbonyl, the rate of that process should be greater than the analogous process involving the all-carbon analog. If, on the other hand, the rates are similar, little change in oxygen or carbon hybridization would be indicated between reactant and transition state.

We have studied the thermal rearrangement of 2,3,4,4-tetramethyloxetene (**1**)[5] to enone **2** in order to compare the results with known cyclobutene–butadiene rearrangements. As shown below, this oxetene rearranges much faster than substituted cyclobutenes and is catalyzed by very small amounts of acid. These results, in part, can be rationalized by the thermodynamic concepts described above.



1 2

The sample of oxetene was prepared[5] by irradiation of 3,4-dimethyl-3-penten-2-one (**2**) through Vycor in pentane followed by bulb-to-bulb vacuum transfer. A uv spectrum of the pentane solution showed a *ca.* 0.095 *M* solution of an 85:15 mixture of oxetene and starting enone. Vpc and nmr analyses showed that no more than *ca.* 1% of other materials was present. Approximately 1-ml aliquots of the photolysis solution were diluted to 50 ml with the various solvents given in Table I and the amount of enone was measured as a function of time at various temperatures (41–61°) by uv spectroscopy between 238 and 245 nm. In all runs the theoretical amount of enone reappeared. First-order rate constants were calculated by a weighted least-squares computer program which accounted for random errors in both time and optical density. Representative rate constants in heptane solution are given in Table II.

Table I. Kinetics and Activation Parameters for Rearrangement of 2,3,4,4-Tetramethyloxetene (**1**) in Different Solvents[a]

Solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	10^6k, sec^{-1}, 25°
Heptane[b]	25.09 ± 0.68	−1.4 ± 2.1	1.26 ± 0.11
Acetonitrile[c]	24.03 ± 0.86	−0.5 ± 2.7	11.82 ± 1.0
tert-Butyl alcohol[d]	24.64 ± 1.03	3.0 ± 3.3	23.90 ± 2.0

[a] All errors are standard deviations with two degrees of freedom; rate constants at 25° were calculated from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. [b] Mallinckrodt "Spectrar" grade. [c] Distilled from P_2O_5. [d] Distilled from CaH_2.

Table II. First-Order Rate Constants for Rearrangement of Oxetene **1** in Heptane[a] Solution

Temp, °C[b]	10^5k, sec^{-1} [c]	DF[d]
41.11	1.15 ± 0.03	10
49.95	3.72 ± 0.10	8
61.59	14.2 ± 0.5	8

[a] Mallinckrodt "Spectrar" grade. [b] ±0.02°. [c] Errors are standard deviations. [d] Internal degrees of freedom obtained by analyzing successive reaction aliquots throughout the kinetic run.

Eyring activation parameters were calculated by a similar least-squares program which accounted for random errors in both rate constant and temperature; see Table I.

The small solvent effects are consistent with a simple electrocyclic rearrangement with little charge separation. Similar small solvent effects were observed in substituted cyclobutene rearrangements to butadiene.[6]

Since *tert*-butyl alcohol has the same Z value[7] and a lower dielectric constant than acetonitrile, the increased rate in *tert*-butyl alcohol might be due to hydrogen bonding of the hydroxyl group to the oxetene. Since this explanation suggested that the rearrangement would be strongly acid catalyzed, a 30-μl portion of 10^{-2} *M* $HClO_4$ in acetonitrile was added to a 3-ml portion of 0.005 *M* oxetene in *tert*-butyl alcohol. In less than 2 min a uv spectrum showed complete reappearance of the enone. To ensure that the neutral rearrangement in *tert*-butyl alcohol was not catalyzed by stray sources of acid, the rate was determined in *tert*-butyl alcohol with an added 75 mol excess of undissolved sodium carbonate. At 37.48°, the rate constant was $1.46 \pm 0.02 \times 10^{-4}$ sec^{-1}. This value should be compared to a calculated neutral *tert*-butyl alcohol value at 37.48° of $1.32 \pm 0.03 \times 10^{-4}$ sec^{-1}.

In conclusion, the substitution of a methylene group of a cyclobutene by an oxygen atom tremendously increases the reactivity of the molecule toward rearrangement. The rearrangement kinetics of the analogous 1,2,3,3-tetramethylcyclobutene is unknown, but the gas-phase rearrangement of the isomeric *cis*-1,2,3,4-tetramethylcyclobutene has an enthalpy and entropy of rearrangement of 36.37 ± 0.46 kcal/mol and 2.9 ± 1.0 eu, respectively (7 DF).[8] Comparison of the extrapolated rate of rearrangement at 25° for this tetramethylcyclobutene with that of tetramethyloxetene **1** shows that substitution of an oxygen atom in cyclobutenes produces a rate acceleration of *ca.* 10^7.

(4) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(5) L. E. Friedrich and G. B. Schuster, *J. Amer. Chem. Soc.*, **91**, 7204 (1969).

(6) (a) R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H.-A. Brune, *Chem. Ber.*, **98**, 2339 (1965); (b) H. M. Frey, *Trans. Faraday Soc.*, **59**, 1619 (1963); (c) H. M. Frey, D. C. Montague, and I. D. R. Stevens, *ibid.*, 63, 372 (1967).

(7) E. M. Kosower in "Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 301.

(8) Calculated from the data of G. R. Branton, H. M. Frey, and R. F. Skinner, *Trans. Faraday Soc.*, 62, 1546 (1966).

The enthalpy of activation for rearrangement of oxetenes is *ca.* 10 kcal/mol less than for cyclobutenes, presumably because the oxetene rearrangement to product is more exothermic. Use of Franklin group equivalents with equal strain for the tetramethyloxetene and cyclobutene[9] shows that the oxetene rearrangement liberates *ca.* 23 kcal/mol more energy than the cyclobutene rearrangement. The results show that approximately half of this extra product stabilization is reflected in a lower transition energy for reaction.

Acknowledgment. The authors wish to thank the National Science Foundation for support of this work and the Computing Center of the University of Rochester for use of their facilities.

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(9) In general, rings containing oxygen have the same strain as their all-carbon analogs; see A. S. Pell and G. Pilcher, *Trans. Faraday Soc.*, **61**, 71 (1965).

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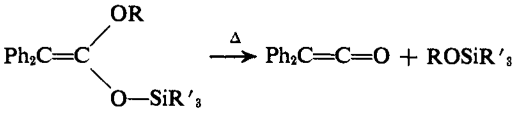
Pyrolysis Studies of Ketene Alkyl Trialkylsilyl Acetals

Sir:

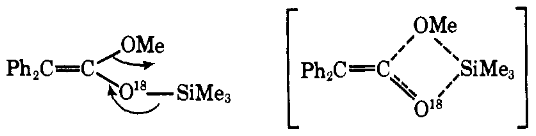
We have found that diphenylketene methyl trimethylsilyl acetal[1] (**1**, R = R′ = Me), at reflux at *ca.* 180° and 30 Torr for 30 min, is converted[2] to diphenylketene in 85% yield. Indeed, the synthetic sequence methyl diphenylacetate to **1** to diphenylketene can be rapidly accomplished in 80% overall yield and it seems to be the method of choice for the synthesis of this compound.[3] Other diarylketenes including *p*-tolyl and fluorene have been similarly prepared. Compound **1** (R = R′ = Et) on pyrolysis gave diphenylketene in 35% yield.[4]



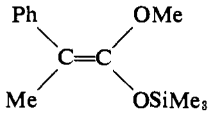
$$\mathrm{Ph_2C{=}C(OR)(O{-}SiR'_3)} \xrightarrow{\Delta} \mathrm{Ph_2C{=}C{=}O + ROSiR'_3}$$

1

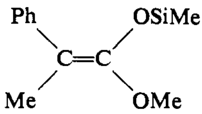
To elucidate the mechanism of this reaction a mixture of **1** (R = R′ = Me) and **1** (R = R′ = Et) was thermolyzed and the ether fraction was shown to contain only $\mathrm{MeOSiMe_3}$ and $\mathrm{EtOSiEt_3}$. This negative crossover result eliminates free-radical and intermolecular mechanisms and is compatible with an intramolecular pathway. To answer the question as to which oxygen bond was cleaved in the process, the $^{18}\mathrm{OSiMe_3}$ acetal was pyrolyzed and ^{18}O-diphenylketene was exclusively obtained.[5] Thus, the mechanism is consistent with a four-center one[6] featuring a methoxyl migration to silicon with concomitant ketene formation. The transition state is probably accommodated by the ability of silicon to increase its coordination number involving 3d orbitals.[7]



The pyrolysis of the isomers **2a** and **2b** shown below proved to be of special interest. The cis isomer **2b** (phenyl and trimethylsilyl)[8] was stable at 190° and 150 Torr for 0.5 hr but at 220° for 2 hr was converted to methylphenylketene.[9] The trans isomer **2a** at 190° for 0.5 hr formed methylphenylketene.[9] Thus **2b** with the methoxyl group trans to phenyl is more stable.[10]

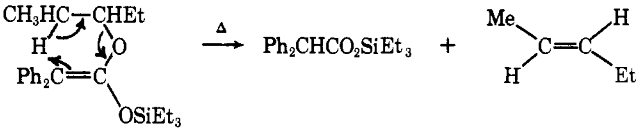


2a

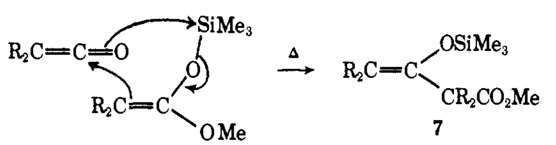


2b

The thermolysis of **1**, R = 3-pentyl, R′ = Et, took a different course[2] yielding triethylsilyl diphenylacetate and *trans*-2-pentene. These products may form *via* the indicated six-center transition state.



Pyrolysis studies were also carried out using hydrogen aryl and dialkylketene acetals of the type RR′C=C-(OMe)$\mathrm{OSiMe_3}$; **3**, R = H, R′ = Ph; **4**, R = R′ = Me; **5**, R = R′ = $\mathrm{(CH_2)_4}$; and **6**, R = R′ = $\mathrm{(CH_2)_5}$. Several of these compounds gave products represented by **7** which are called ketene–ketene acetal addition products. Their formation is visualized as arising from a six-center reaction involving initially formed ketene and starting material.[11] Such a reaction would be expected to have rigid stereochemical requirements. Thus, where R = phenyl the reaction failed to occur and diphenylketene was the product of pyrolysis. Pyrolysis of compound **3** at 180° and 30 Torr gave a 90% yield of **7a**,[12] the stereochemistry of which is established as having phenyl and $\mathrm{OSiMe_3}$ cis.[13] This reaction is in accord with **3** having phenyl and *O*-trimethylsilyl groups trans as shown below.



7

Compound **4** heated in a sealed tube at 210° for 4 hr gave a 90% yield of product consisting of 20% di-

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(1) Y. N. Kuo, F. Chen, C. Ainsworth, and J. J. Bloomfield, *Chem. Commun.*, 136 (1971).

(2) For a reference concerning the pyrolysis of ketene acetals see S. M. McElvain, H. I. Anthes, and S. H. Shapiro, *J. Amer. Chem. Soc.*, **64**, 2525 (1942). Ketene diethyl acetal heated at 200° gave ethyl acetate and ethylene.

(3) L. I. Smith and H. H. Hoehn, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 356.

(4) The major product of the reaction is triethylsilyl diphenylacetate and ethylene. See ref 2.

(5) Determined by mass spectral analysis. The mass spectrum of 1, R = R′ = Me, showed an equal distribution of heavy oxygen in diphenylketene and ether.

(6) A heterolytic cleavage involving a tight ion pair is not excluded.

(7) F. P. Boer and F. P. van Remoortere, *J. Amer. Chem. Soc.*, **92**, 801 (1970), and references cited.

(8) Y. N. Kuo, F. Chen, and C. Ainsworth, *Chem. Commun.*, 137 (1971).

(9) The yield was about 30% accompanied with dimer and polymer.

(10) Experiments which have a bearing on this finding are in progress.

(11) (a) G. S. Burlachenko, Y. I. Baukov, and I. F. Lutsenko, *J. Gen. Chem. USSR*, **40**, 88 (1970); (b) R. Scarpati, *Rend. Accad. Sci. Fis. Mat., Naples*, 154 (1962).

(12) New compounds gave acceptable elemental analyses and molecular peaks in mass spectral analysis.

(13) The $\mathrm{SiMe_3}$ signal was at δ 0.0 ($\mathrm{CCl_4}$); see ref 8.