Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

KETENE ALKYLTRIALKYLSILYL ACETALS: SYNTHESIS, PYROLYSIS AND NMR STUDIES

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(Received March 24th, 1972)

SUMMARY

Two general methods of synthesis of ketene alkyltrialkylsilyl acetals (I) have been developed. The first was by reaction of disubstituted malonates and sodium/xylene, and the other method was by reaction of the α-anion of substituted acetates with trimethylchlorosilane. Carbomethoxy ketene methyltrimethylsilyl acetals (III) were also prepared. Pyrolysis of diaryl ketene methyltrimethylsilyl acetals gave diaryl ketenes in good yield. The mechanism of this reaction has been established as intramolecular employing ^{18}O. Alkyl, aryl and dialkyl ketene methyltrimethylsilyl acetals on pyrolysis gave ketene–ketene acetal addition compounds (II). Spectral studies of aryl ketene acetals (I) are consistent with a dipolar structure $Ar_2C^- - C^+(OMe)OSiMe_3$. The general conclusion is made that freedom of rotation about a carbon–carbon double bond is determined by the attached substituents. Spectral studies are in agreement with fluxional behavior of compounds (III) in which the carbomethoxy and trimethylsilyloxy groups are *cis*. The results of mass fragmentation of ketene acetals (I) are similar to their thermolytic cleavage. Interestingly, however, ketene–ketene acetals (II) in the mass spectrometer are fragmented into the ketene and ketene acetal fragments from which molecules they are thermally formed.

INTRODUCTION

Ketene acetals have been known since 1907 and the literature on them is quite extensive[1,2] due largely to the work of McElvain. The first ketene trialkylsilyl acetal recognized as such was prepared by Petrov[3] in 1959 by the reaction of triethylsilane and methylacrylate.

$$Et_3SiH + CH_2{=}CHCO_2Me \rightarrow CH_3CH{=}C(OMe)OSiEt_3$$

Hauser[4] was the first to treat α-anions of acetates with trimethylchlorosilane (TMCS) and he formulated the product as a *C*-silated one. Later, Rochow[5] using TMCS and the anion of ethyl acetate found both *C*- and *O*-silated products.

$$\overline{CH}_2CO_2Et + TMCS \rightarrow Me_3SiCH_2CO_2Et + CH_2{=}C(OEt)OSiMe_3$$

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Interestingly, Lutsenko *et al.*,[6] were able to control *C*- and *O*-silation by solvent variation using mercuric salts of acetates. Furthermore, they were able to rearrange the

$$Hg(CH_2CO_2Me)_2 + Et_3SiI \xrightarrow{CCl_4} CH_2{=}C(OMe)OSiEt_3$$
$$Hg(CH_2CO_2Me)_2 + Et_3SiI \xrightarrow{CHCl_3} Et_3SiCH_2CO_2Me$$

O-silated acetal to *C*-silated product using mercuric iodide.

$$CH_2{=}C(OMe)OSiEt_3 \xrightarrow{HgI_2} Et_3SiCH_2CO_2Me$$

We were led into the field of ketene alkyltrialkylsilyl acetals when studying the reaction of disubstituted malonic esters and sodium/xylene[7]. In this reaction, run in the presence of TMCS, carbon monoxide was evolved and ketene methyl trimethylsilyl acetal was formed in high yield*. The products so prepared by this reaction are described in a preliminary publication[8]. The utility of the reaction lies in the fact

$$R_2C(CO_2Me)_2 \xrightarrow[TMCS]{Na} R_2C{=}C(OMe)OSiMe_3 + CO + MeOSiMe_3$$

that ketene alkyltrialkylsilyl acetals are readily solvolyzed by methanol and give methyl acetates, quantitatively. Thus, the sequence represents a decarboalkoxylation of malonates to acetates**.

RESULTS AND DISCUSSION

Synthesis of ketene alkyltrialkylsilyl acetals (I)

We have found that ketene alkyltrialkylsilyl acetals (I) (Table 1) are best prepared from α-anions of acetates and TMCS according to two general methods which

$$RR'CHCO_2Me \xrightarrow{LDA} RR'\bar{C}CO_2Me \xrightarrow{TMC} \underset{(I)}{\overset{R}{\overset{R'}{}}\!\!>C{=}C\!<\!\overset{OMe}{\underset{OSiMe_3}{}}}$$

are designated Methods 1 and 2. This procedure not only involved fewer steps and gave better yields than the disubstituted malonic ester–sodium method but had greater variation in R-substituents.

Method 1. Lithium diisopropylamide (LDA) was prepared at 0° from diisopropylamine and n-butyl lithium[9]. Ester was added at 0° followed by addition of TMCS. The products were obtained by distillation in 90–95% yield***, and are described in Tables 1 and 2.

Method 2. It was found that the α-anions of methyl acetate and monoalkyl acetates were very reactive at 0° and condensation took place. Thus, in Method 2 the lithium diisopropylamide was formed at 0° in THF, then cooled to −78°, ester was added and after 30 min TMCS was slowly added.

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* Proposals concerning the mechanism have been advanced[8].

** Also recognized by Krollpfeiffer and Rosenberg[7].

*** Details of the method are given in the Experimental Section.

TABLE 1

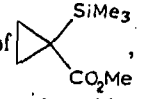
KETENE ALKYL TRIALKYLSILYL ACETALS (I), RR'C=C(OR'')OSiR'''$_3$

Compound	R	R'	R''	R'''	Yield (%)	b.p. (°C/mm)	Method	Formula	Analysis (%)			
									Found		Calcd.	
									C	H	C	H
I-1[a]	H	H	Me	Me	45[b]		2					
I-2[a,c]	H	Me	Me	Me	90		2					
I-3	H	t-Bu	Me	Me	90	45/0.5	2	$C_{10}H_{22}O_2Si$	60.02	10.95	59.37	10.96
I-4	Me	Me	Me	Me	95	35/15	1	$C_8H_{18}O_2Si$	54.92	10.22	55.12	10.41
I-5	$-(CH_2)_2-$		Me	Me	10[d]		2[e]	$C_8H_{16}O_2Si$				
I-6	$-(CH_2)_4-$		Me	Me	95	78/3	1	$C_{10}H_{20}O_2Si$	59.93	10.11	59.97	10.07
I-7	$-(CH_2)_5-$		Me	Me	95	80/2.5	1	$C_{11}H_{22}O_2Si$	61.95	10.46	61.65	10.35
I-8	H	Ph		Me	95	95/0.5	1	$C_{12}H_{18}O_2Si$	64.61	8.21	64.82	8.16
I-9	Me	Ph	Me	Me	90[f]	76/0.1	1	$C_{13}H_{20}O_2Si$	65.93	8.76	66.05	8.53
I-10	Ph	Ph	Me	Me	95	155/0.25	1	$C_{18}H_{22}O_2Si$	71.53[g]	7.59	72.43	7.43
I-11[h]	Ph	Ph	Me	Me	95	155/0.25	1		[g]			
I-12	Ph	Ph	Et	Et	95	153/0.01	1		[g]			
I-13	Ph	Ph	Et_2CH	Et	95	165/0.01–0.1[i]	1		[g]			
I-14	[j]	[j]	Me	Me	95	165/0.6	1		[g]			
I-15	[k]		Me	Me	95	160/0.5[i]	1		[g]			

[a] Reported (ref. 6).

[b] Contains an equal amount of $Me_3SiCH_2CO_2Me$ (*cf.* ref. 6).

[c] No *C*-silation

[d] Contained in a 40% yield of 

, b.p. 54° 10 mm; NMR (CCl_4) δ 0.00 (s, 9 H), 0.5–0.8 (m, 2 H), 0.9–1.2 (m, 2 H), 3.6 (s, 3 H). Compound I RR'=$(CH_2)_3$ was obtained in 50% yield together with a 25% yield of the *C*-silation compound by Method 2.

[e] See special conditions, Method 2 (Experimental Section).

[f] Contains both isomers.

[g] Analytical samples were contaminated with ketene.

[h] $^{18}OSiMe_3$ labeled.

[i] Compound decomposed on distillation.

[j] *p*-$CH_3C_6H_4$

[k] RR'=9-fluorene

TABLE 2

SPECTRAL MEASUREMENTS FOR COMPOUNDS(I), $RR'C{=}C\begin{matrix}OMe\\OSiMe_3\end{matrix}$

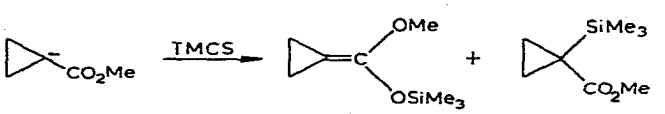
Compound	*NMR data (CCl_4), δ values*					*IR C=C stretch*	*UV (hexane)*	
	$Si(CH_3)_3$	OCH_3	CCH_3	C_6H_5	*H*	(cm^{-1})[a]	λ_{max}	$\varepsilon \times 10^4$
I-3	0.18	3.45	1.02		3.58	1670		
I-4	0.18	3.48	1.48, 1.54			1708		
I-5	0.19	3.66	[b]			1785		
I-6	0.20	3.48	[c]			1710		
I-7	0.20	3.48	[d]			1700		
I-8a[e]	0.29	3.65		6.9–7.4 (m)	4.62	1640–1660	268	1.42
I-8b	0.26	3.60		6.9–7.4 (m)	4.52			
I-9a[f]	0.25	3.40	1.86	7.0–7.4 (m)		1650–1670		
I-9b	−0.02	3.60	1.90	7.25			260	0.84[g]
I-10	0.03	3.50		7.20		1630	267	1.32
I-11	0.03	3.50		7.20				
I-12[h]								
I-13[i]								
I-14	0.03	3.48	2.30	6.99		1635		
I-15	0.39	3.92		[j]		1638		

IR data (neat). Bands are strong unless otherwise designated.

I-8a 3020 m, 2960, 1775 m, 1650, 1600, 1440, 700, cm^{-1}
I-8b Like I-8a with additional bands at 1060, 930 cm^{-1}

[a] Strong band at 860–870 cm^{-1} with overtone at 1720–1740 cm^{-1}. See refs. 5 and 20 for related compounds.
[b] δ 1.4 (t, $(CH_2)_2$).
[c] 1.4–1.7 (m, 4 H), 1.9–2.4 (m, 4 H).
[d] 1.4–1.6 (m, 6 H), 1.8–2.2 (m, 4 H).
[e] Obtained as a pure isomer. The stereochemistry of I-8a and I-8b is not assigned.
[f] Obtained as a mixture. Isomer (a) designates the phenyl and $OSiMe_3$ groups *trans*.
[g] Contains 30% of isomer (a).
[h] 0.3–1.2 (m, 19H), 3.78 (q, 2 H), 7.2 (s, 10 H).
[i] 0.4–1.1 (m, 21 H), 1.45 (q, 4 H), 4.83 (m, 1 H), 7.16 (s, 10 H).
[j] 7.1–7.4 (m, 4 H), 7.6–7.9 (m, 4 H).

Methyl acetate anion gave about a 50/50 mixture of *C*- and *O*-silated products. When methyl cyclopropane carboxylate and LDA were allowed to react only 10 min at −78° followed by addition of TMCS (special conditions), a 10% yield of ketene silyl acetal was formed. The main product was the *C*-silylated material shown below:



Interestingly, methyl t-butylacetate gave only *O*-alkylation, probably due to steric factors.

Carbomethoxy ketene methyltrimethylsilyl acetals (III) (Table 6) were readily prepared[10] from monosubstituted malonates using sodium hydride–dimethoxyethane (DME), and for organizational purposes the procedure is designated *Method* 3.

$$RCH(CO_2Me)_2 \xrightarrow[TMCS]{NaH-DME} MeO_2C\diagup\!\!\diagdown C=C(OMe)OSiMe_3$$
(III)

(R = H, Me, CO_2Me and Ph)

There is the possibility of isomers for (III) and NMR studies indicated their presence where R = Ph.

Pyrolysis of ketene alkyl trialkylsilyl acetals(I)

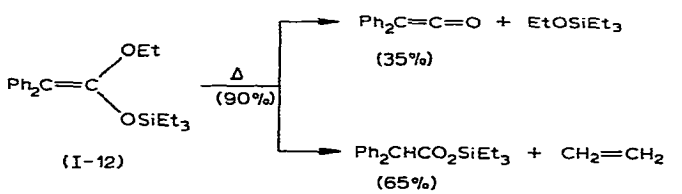
We were led into a thermolysis study of compounds (I) by the fact that certain of the compounds were unstable to distillation. It was difficult to obtain an analytical sample of compound I-10 and the distilled product contained diphenyl ketene. On the other hand, aliphatic ketene acetals were generally stable to distillation at atmospheric pressure and thermolysis studies were carried out in sealed tubes. A preliminary report of the study has appeared[11].

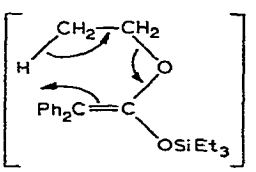
Diaryl ketene acetals (I) on heating are converted in high yield to diaryl ketenes. The synthetic sequence of methyldiphenyl acetate to I-10 (Table 1) to diphenyl ketene

$$Ar_2C=C\diagup\!\!\diagdown\begin{matrix}OR\\OSiR'_3\end{matrix} \xrightarrow{\Delta} Ar_2C=C=O + ROSiR'_3$$

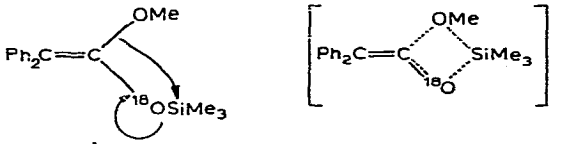
can be accomplished rapidly in about 80% overall yield and it is probably the method of choice for the synthesis of this compound[12]. Details concerning the conditions of the reaction are given in the Experimental Section.

Compound I-12 (Table 1) on pyrolysis gave diphenyl ketene in 35% yield and triethylsilyl diphenylacetate. The formation of the latter compound is visualized as a six-center reaction and is similar to the finding of McElvain[13] for the pyrolysis of ketene diethyl acetal.





The mechanism of formation of diphenyl ketene from I-10 and I-12 was shown by crossover results to be intramolecular[11]. Results from the pyrolysis of I-11 (^{18}O-$SiMe_3$) are consistent with a four-center mechanism illustrated below.



The transition state is probably stabilized by *d*-orbital overlap of silicon.

Thermolysis of hydrogen–aryl and dialkyl ketene acetals of the type RR'C=C-(OMe)OSiMe$_3$ gave products (II) (Tables 3 and 4) which we have called ketene–ketene acetal addition products. Their formation via a six-center reaction involving initially formed ketene and starting material is shown below ***.

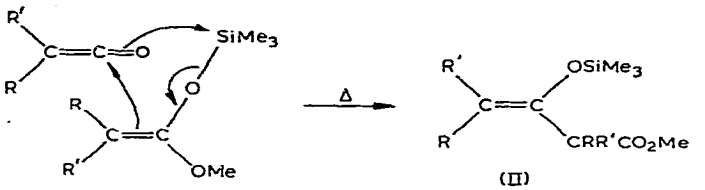


TABLE 3

KETENE–KETENE ACETAL ADDITION COMPOUNDS (II), RR'C=C(OSiMe$_3$)CRR'CO$_2$Me

Compound	*R*	*R'*	*Yield (%)*	*b.p. (°C/mm)*	*Formula*	*Analysis (%)*			
						Calcd.		*Found*	
						C	*H*	*C*	*H*
II-1	Me	Me	75	95/5	$C_{12}H_{24}O_3Si$	58.99	9.90	58.37	9.75
II-2	$-(CH_2)_4-$		75	89/0.02	$C_{16}H_{28}O_3Si$	64.83	9.52	65.94	9.24
II-3	$-(CH_2)_5-$		75	110/0.01	$C_{18}H_{32}O_3Si$	66.63	9.90	65.91	9.54
II-4	H	Ph	85	130/0.05	$C_{20}H_{24}O_3Si$	70.57	7.11	69.88	7.11

TABLE 4

NMR SPECTRAL DATA FOR COMPOUNDS (II), R'$_b$(OSiMe$_3$)C=C(R$_a$)CRR'CO$_2$Me$_{cd}$

Compound	*NMR data (CCl_4), δ values*					
	a	*b*	*c*	*d*	*CO_2Me*	*$SiMe_3$*
II-1	1.56	1.41	1.25	1.25	3.62	0.20
II-2	1.4–2.4 (m, 16 H)				3.62	0.20
II-3	1.3–2.2 (m, 20 H)				3.62	0.20
II-4	5.53	7.1–7.4 (m)	4.40	7.3 (s)	3.68	0.00

* Burlachenko *et al.* established the intermediacy of the ketene[14].

** The products from the reaction of diphenyl ketene and ketene acetals[2] should probably be reformulated according to this mechanism.

TABLE 5

β-KETO ESTERS (IV), $\overset{a}{R}\overset{b}{R'}CHCOC\overset{c}{R}\overset{d}{R'}CO_2Me$ AND THEIR NMR DATA
NMR chemical shift δ values (CCl_4) at ambient temperature

Compound	*R*	*R'*	*a*	*b*	*H*	*c*	*d*	*CO_2Me*
IV-1[a]	Me	Me	1.06 (d)	1.06 (d)	2.82 (m)	1.21	1.21	3.70
IV-2	$-(CH_2)_4-$		1.4–2.3 (m)		2.4–2.7 (m)	1.4–2.3 (m)		3.61
IV-3	$-(CH_2)_5-$		1.3–2.2 (m)		2.3–2.6 (m)	1.3–2.2 (m)		3.62
IV-4[b]	H	Ph	3.62	7.3 (s)	3.62	4.62	6.9–7.3 (m)	3.62

[a] Reported by Levine and Hauser[25]. [b] m.p. 68°.

TABLE 6

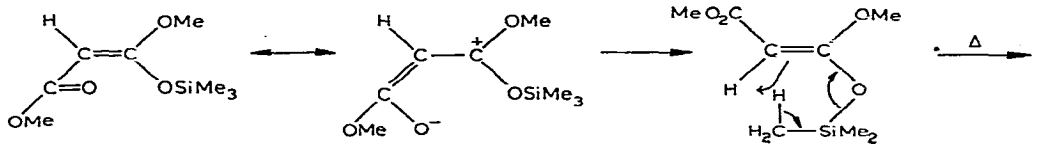
COMPOUNDS III, $R(MeO_2C)C{=}C(OMe)(OSiMe_3)$ AND THEIR SPECTRAL DATA

Compound[a]	*R*	*b.p.* (°C/mm)	*NMR data (CCl_4), δ values*						*IR C=C stretch* (cm^{-1})
			$SiMe_3$	*OMe*	*CMe*	*Ph*	*CO_2Me*	*H*	
III-1a[b]	H	90/1.4	0.27	3.58			3.58	4.25	1600
III-2a[c]	Me	60/0.25	0.29	3.52	1.66		3.52		1600 (br)
III-3[d]	CO_2Me	120/0.5	0.35	3.65			3.65		1530 (br)
III-4a[e]	Ph	118/0.05	0.37	3.50		7.15	3.50		1560 (br)
III-4b[e]	Ph		0.02	3.55		7.20	3.75		

[a] Isomer (a) designates CO_2Me and $OSiMe_3$ groups *cis*. Compounds III-1a and III-2a were erroneously designated 1b and 2b in ref. 10.
[b] Anal.: Found: C, 47.21; H, 8.02. $C_8H_{16}O_4Si$ calcd.: C, 47.03; H, 7.90%.
[c] Anal.: Found: C, 49.77; H, 8.02. $C_9H_{18}O_4Si$ calcd.: C, 49.51; H, 8.31%.
[d] Anal.: Found: C, 49.51; H, 8.31%. $C_{10}H_{18}O_6Si$ calcd.: C, 45.78; H, 6.91%.
[e] The crude isomer mixture was used since the product underwent change on distillation at reduced pressure. Isomer (b) designates CO_2Me and $OSiMe_3$ groups *trans*.

Aliphatic ketene acetals I-4, I-6 and I-7 on pyrolysis gave compounds (II) plus about a 20% yield of dialkyl ketene dimer[11]. Compounds (II) readily solvolyzed using methanol containing a catalytic amount of hydrochloric acid to give β-keto esters (IV) (Table 5) in almost quantitative yield.

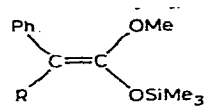
The pyrolysis of compounds (III) was more complex. As an example, III-1a (Table 6, CO_2Me and $OSiMe_3$ groups *cis*), heated in a sealed tube at 95° for 25 h gave methyltrimethylsilyl ether and a 30% yield of dimethylmalonate. The formation of the latter compound is particularly interesting. It is visualized as involving an unsaturated silicon intermediate[15] which polymerized rapidly.



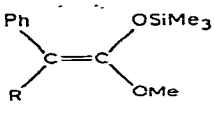
$CH_2(CO_2Me)_2 + [CH_2{=}SiMe_2]$

Spectroscopic studies

1. *NMR studies.* The NMR data for compounds (I) are shown in Table 2 and arguments for the analysis of the spectra have been advanced[10]. Compound (I) can exist in isomeric forms in which the phenyl and $OSiMe_3$ groups are *trans* (Ia) or *cis* (Ib).



(Ia)

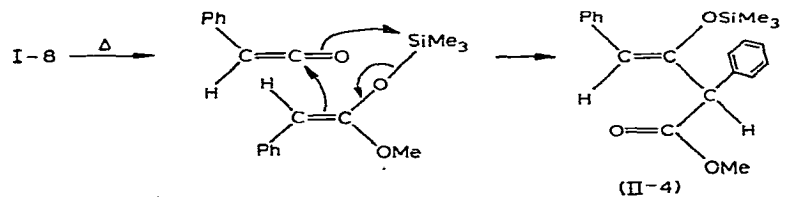


(Ib)

We believe that the system is best analyzed in terms of the phenyl signal appearing as a singlet when not coplanar with the ene and as a multiplet when coplanar[16]. Thus, when R = H (I-8), the phenyl is a multiplet and methyl signals of the $SiMe_3$ group of both isomers are at the relatively low field values of δ 0.29 and 0.26. Where R = Me, the phenyl signal of I-9a is a multiplet, indicating coplanarity, whereas for I-9b, the phenyl signal is a singlet, indicating non-coplanarity accompanied by upfield shifting of the $SiMe_3$ signal due to shielding by the phenyl.

Compound I-10 (R = Ph) at room temperature has a single phenyl signal consistent with freedom of rotation about the carbon–carbon double bond system[17] and represented by the dipolar form $Ph_2C^- - C^+(OMe)OSiMe_3$.

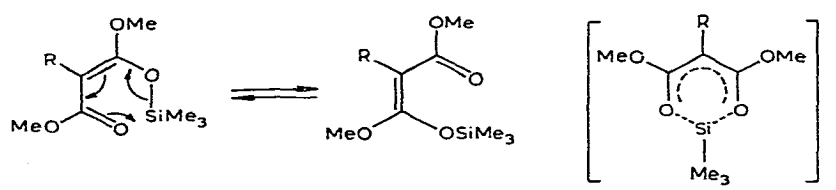
The favored stereochemistry for the formation of II-4 (R = H, R′ = Ph) from I-8 would be the less sterically hindered one shown*.



(II-4)

The NMR spectrum of II-4 (Table 4) seems incongruous with the structure assigned in terms of earlier arguments, namely, the phenyl attached to the ene system should be coplanar and therefore the $SiMe_3$ signal should have a low value rather than the high value observed. Perhaps the high shift value results from the $SiMe_3$ protons experiencing the positive shielding region of the phenyl group of the $CHPhCO_2Me$ moiety.

NMR data for compounds (III) are shown in Table 6. The main feature of the spectra is the equivalency of the OMe and CO_2Me signals. This we have attributed to a *cis* arrangement of CO_2Me and $OSiMe_3$ groups enjoying fluxional behavior[10,18] or topomerization[19]. The structure is best represented by the bracketed formula shown.



* Unfortunately, these arguments do not establish the stereochemistry of I-8a.

The *cis* arrangement is designated isomer IIIa. Compound III-4b (R = Ph) with a *trans* arrangement of CO_2Me and $OSiMe_3$ groups has different methyl signals for the OMe and CO_2Me groups.

2. *IR and UV studies.* The IR and UV data for compounds (I) are given in Table 2. The C=C stretch band of compound I-4 at 1708 cm^{-1} is relatively high and about the same value as that reported for dimethyl ketene dimethyl acetal*. The phenyl compound I-10 at 1630 cm^{-1} is also relatively high compared with ordinary olefins conjugated with phenyl. The value indicates a low degree of conjugation.

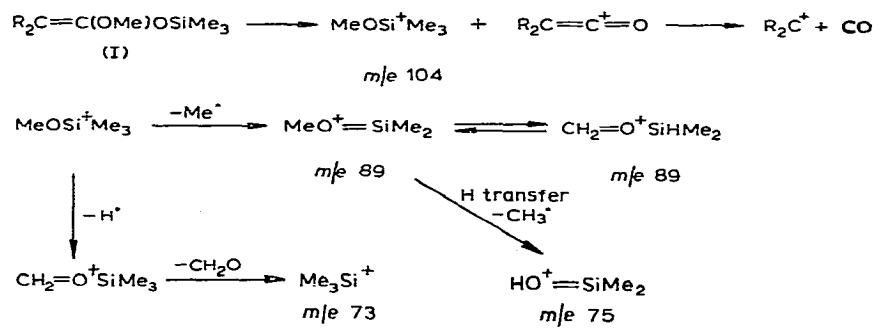
The extinction coefficient value for the UV of I-8a, R = Ph, R′ = H, is near that of phenyl ketene acetal**. The values for I-9a, R = Ph, R′ = Me and I-10, R = R′ = Ph, are lower than that of I-8a, in agreement with the conclusion from the NMR data that I-9a and I-10, in contrast with I-8a, are not coplanar.

The IR data for compounds (III) are given in Table 6. The low C=C stretch bands are indicative of conjugation with ester carbonyl.

Analysis of the IR, UV, and NMR data for compounds I and III leads to the conclusion that freedom of rotation about a carbon–carbon bond is influenced by the substituents attached to the double bond. The rigidity is decreased as electron donating groups (*e.g.*, OR) are located on one carbon atom while electron attracting groups (*e.g.*, CO_2R) are attached to the other atom of the double bond. The decrease of carbon–carbon double bond character can result in freedom of rotation at room temperature.

3. *Mass spectral studies.* The mass spectra of compounds of type I generally show parent ion followed by a peak arising from loss of methyl. Hydrogen transfer and loss of methyl is then repeated to give peaks $M-29$ and $M-43$. The general fragmentation proposed for compounds (I) is given in Scheme 1. It is similar to the mass spectral findings of House[22] and Stork[23] for trimethylsilyl enol ethers.

SCHEME 1



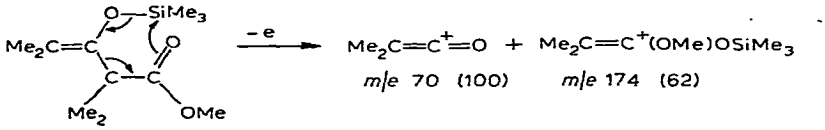
The base peak can be that of ketene (I-4) or ketene minus carbon monoxide (I-9), but it is often 73 or 89. Thus, the electron fragmentation often parallels thermal cleavage. In I-6, *m/e* 147 (50) is a prominent peak which we attribute to the intermolecularly formed species $Me_3SiO^+SiMe_2$[24].

* McElvain and Stern[20] report the carbon–carbon double bond stretch frequency of dimethylketene dimethylacetal at 1710 cm^{-1}.

** Baldwin and Walker[21] reported phenyl ketene acetals as having λ_{max} 265 nm (ε 16000–17000) values.

The mass spectra of ketene–ketene acetal addition compounds (II) are of interest in that the results show fragments that are the reverse of their formation by the thermolysis of compounds (I). Thus, II-1 on mass fragmentation decays according to Scheme 2. The result is another example of a migration of the trimethylsilyl group upon electron impact[24].

SCHEME 2



The mass spectra for compounds (III) are unrevealing since the parent ion is not observed and peaks *m/e* 89 and 59 predominate.

EXPERIMENTAL

Melting points were taken on a Fisher–Johns melting point apparatus, boiling points are uncorrected. NMR studies were done using a Varian A-60A Spectrometer equipped with a variable temperature probe. Infrared spectra were taken on a Perkin–Elmer Model 457 Spectrophotometer. Ultraviolet measurements were taken on a Perkin–Elmer Model 402 Spectrophotometer. Mass spectra were measured with an AEI Model MS12 Spectrometer. Microanalyses were done by Midwest Microlab Ltd., Indianapolis, Indiana.

Starting esters

All of the starting esters are known except 3-pentyl diphenylacetate which was prepared from diphenylacetyl chloride and 3-pentanol in THF giving a 95% yield of the ester: b.p. 159°/0.6 mm; NMR (CCl_4) δ 0.82 (q, 9 H), 1.45 (m, 6 H), 4.76 (m, 1 H) 4.91 (s, 1 H), 7.2 (s, 10 H); IR (neat) 1730 cm^{-1}.

$$Ph_2CH\overset{\overset{^{18}O}{\|}}{C}OMe$$

1. *Preparation of* $Ph_2CH\overset{\overset{^{18}O}{\|}}{C}OMe$. The ^{18}O isotope ester was prepared from diphenyl acetyl chloride and $H_2{}^{18}O$ followed by esterification. A solution of 12.6 g (0.055 mole) of diphenylacetyl chloride and 25 ml of THF containing 1 ml of $H_2{}^{18}O$ (10% enrichment) was heated under reflux for 1 h. The solution was concentrated using a rotary evaporator. The residue was dissolved in 100 ml of ether and washed with 100 ml of saturated sodium bicarbonate solution. After standing in a separatory funnel for 2 h, a slight excess of 5 *N* HCl was added. The aqueous layer was washed with three 50 ml portions of ether and the combined ether extract was dried using anhydrous magnesium sulfate. The solution was filtered and the ether evaporated. The residue of ^{18}O enriched diphenylacetic acid was esterified by heating it overnight with 50 ml of methanol containing 10% concd. H_2SO_4. The product was isolated in the usual manner.

2. *Preparation of lithium diisopropylamide (LDA).* A 250 ml round bottom oven-dried flask was equipped with an addition funnel and a magnetic stirrer. The system was swept with helium or dry nitrogen and a solution of 10 g (0.1 mole) of diisopropylamine and 75 ml of dry THF was added. After cooling in an ice bath, a hexane solu-

tion of 50 ml of 2 *M* (0.10 mole) n-butyllithium was added over a 5 min period and the mixture was stirred for an additional 15 min.

Synthesis of ketene alkyl trialkylsilyl acetals (I), $RR'C{=}C(OR'')OSiR'''_3$ (Table 1)

Method 1. To a solution of LDA described above was added 0.1 mole of ester $RR'CHCO_2Me$ over a 5 min period and the stirred solution was maintained at 0° for 30 min. An excess (25 ml, 0.25 mole) of trimethylchlorosilane (TMCS) was added during a 5 min period and the mixture was allowed to warm to room temperature. After stirring for 30 min, the mixture was filtered and the solution was concentrated using a rotary evaporator*. The residue was washed with dry ether and filtration was repeated. After removal of the ether, an oil remained that was distilled under reduced pressure. The products are described in Table 1.

Method 2. Lithium diisopropylamide (0.1 mole) was cooled in a dry-ice–acetone bath and 0.1 mole of ester ($R'CH_2CO_2Me$) was added over a 5 min period. The stirred solution was maintained at −78° for 30 min and 25 ml (0.25 mole) of TMCS was added during a 5 min period. The mixture was allowed to warm to room temperature. After stirring for 30 min, the mixture was filtered and the solution was treated as described in Method 1.

Method 2: *Special conditions.* 0.1 mole of methyl cyclopropanecarboxylate was treated with 0.1 mole of LDA for 10 min at −78° followed by addition of TMCS. After stirring for 10 min at −78°, the mixture was allowed to warm to room temperature and work up was the same as described in Method 1.

Synthesis of carbomethoxy ketene methyl trimethylsilyl acetals (III), $R(MeO_2C)$-$C{=}C(OMe)OSiMe_3$

Method 3. About 20 ml of dry ether was added to 2.5 g (0.06 mole) of sodium hydride (52% oil dispersion). The ether was decanted and the wash procedure was repeated. The sodium hydride and 75 ml of dry, freshly distilled dimethoxyethane (DME) were placed in a 250 ml oven-dried flask and the system was flushed with dry nitrogen. A solution of 0.05 mole of substituted dimethyl malonate and 25 ml of DME was added dropwise. Stirring was continued until the theoretical amount of hydrogen was evolved (1–2 h). An excess of TMCS (10 ml, 0.1 mole) was added. After stirring for 1 h, the mixture was centrifuged since filtration was very slow and the mixture is sensitive to atmospheric moisture. The DME was removed using a rotary evaporator and the product was distilled under reduced pressure. The products prepared are described in Table 6.

Pyrolysis of compounds (I), $RR'C{=}C(OMe)OSiMe_3$

Procedure 1a. 0.05 mole of dialkyl ketene methyltrimethylsilyl acetal was sealed in a 15 ml thick-wall Pyrex tube and placed in an oil bath at 200° for 4h. The tube was cooled to −78° and the vessel was opened. The residue was distilled to give methyl trimethylsilyl ether collected in a dry-ice–acetone trap and a 95% yield of product. It consisted of 80% ketene–ketene acetal addition product (II) (Table 3) and 20% ketene dimer.

The following compounds were pyrolyzed according to Procedure 1a. Compound I-4 gave II-1 as well as tetramethyl-1,3-cyclobutadione: NMR (CCl_4) δ1.28 s.

* A water trap was placed in the system to avoid plugging of the aspirator.

Compound I-6 gave II-2 and bis(tetramethylene)-1,3-cyclobutadione; NMR (CCl_4) δ 1.5–2.1 m. Compound I-7 gave II-3 and bis(pentamethylene)-1,3-cyclobutadione: NMR (CCl_4) δ 1.4–1.9 m.

Procedure 1b. 0.05 mole of aryl ketene methyltrialkylsilyl acetal I was placed in a 25 ml pear-shaped flask equipped with a 10 cm air condenser and a distilling head. The compound was refluxed slowly at 30 mm pressure using an oil bath at 190°. Low boiling methyl trialkylsilyl ether (90% yield) was collected in a trap, cooled with dry-ice–acetone. After 30 min heating, the residue was distilled under reduced pressure. The following compounds were pyrolyzed according to Procedure 1b.

Pyrolysis of I-8. Compound I-8 (11.5 g, 0.05 mole) was heated under the conditions of Procedure 1b for 3 h and compound II-4 (Table 3) was formed.

Pyrolysis of I-9. A mixture consisting of 65% isomers I-9a (Ph and $OSiMe_3$ *trans*) and 35% isomer I-9b (Ph and $OSiMe_3$ *cis*) was heated according to procedure 1b. Some unchanged isomer I-9b was obtained together with a small yield of methylphenyl ketene: b.p. 66°/2 mm; IR (neat) 2100 cm^{-1}. Also obtained was the dimer, 2,4-dimethyl-2,4-diphenyl-1,3-cyclobutadione: m.p. 165° (sub. at 145°); NMR (CCl_4) δ 1.54 (s, 6 H), 7.2–7.7 (m, 10 H); IR (KBr) 1740 cm^{-1}.

When the mixture was heated 2 h under the reaction conditions, both isomers were decomposed and methylphenyl ketene polymer was formed.

Pyrolysis of I-10. Compound I-10 gave diphenyl ketene in 85% yield. The NMR showed only aromatic protons and the compound reacted with water to give diphenylacetic acid in quantitative yield. Diphenyl ketene: b.p. 85°/0.2 mm; NMR (CCl_4) δ7.25 s; IR (neat) 2100 cm^{-1}; mass spectrum *m/e* (rel. intensity) 194 (80), *M*, 167 (20), 166 (100), 165 (70), 82.5 (10).

Pyrolysis of I-11. Compound I-11 (2 g) gave a 90% yield of methyl trimethylsilyl ether and an 85% yield of $Ph_2C{=}C{=}{}^{18}O$. Mass spectral data of the product compared with natural diphenyl ketene showed it to be 4% ^{18}O enriched, with no ^{18}O enrichment in the methyl trimethylsilyl ether. Mass spectral analysis of I-11 showed an equal distribution of ^{18}O between diphenyl ketene and methyl trimethylsilyl ether.

Pyrolysis of I-12. Compound I-12 gave diphenyl ketene and ethyl triethylsilyl ether in 35% yield. Triethylsilyl diphenylacetate was also obtained in 60% yield.

Pyrolysis of a mixture of I-10 and I-12. A mixture of equimolar quantities of I-10 and I-12 gave diphenyl ketene, triethylsilyl diphenylacetate and an ether fraction shown by GLC to be only methyl trimethylsilyl ether and ethyl triethylsilyl ether as shown by comparison with authentic samples. Equimolar quantities of I-10 and I-12 were injected into a GLC Carbowax column at an injection temperature of 200° and the ether fraction contained only the two above ethers.

Pyrolysis of I-13. Compound I-13 was only obtained crude since on distillation under reduced pressure it gave *trans*-2-pentene and 90% yield of triethylsilyl diphenylacetate: NMR (CCl_4) δ 0.95 (t, 3 H), 1.5–1.7 (m, 2 H), 1.8–2.3 (m, 2 H), 5.2–5.5 (m, 2 H). The *trans*-2-pentene was identical with authentic material.

Pyrolysis of I-14. Compound I-14 gave an 85% yield of methyl trimethylsilyl ether and a 50% yield of di-*p*-tolyl ketene : b.p. 150°/0.6 mm; NMR (CCl_4) δ 2.35 (s, 6 H), 7.05 (s, 4 H); IR (Nujol) 2108, 1745, 1374, 1260 cm^{-1}.

Pyrolysis of I-15. Crude I-15 on thermolysis was converted in about 50% yield to 9-fluorene ketene: NMR (CCl_4) δ 7.1–7.4 (m, 4 H), 7.6–7.9 (m, 4 H).

Pyrolysis of compounds (III). Preliminary pyrolysis studies of compounds (III) indicated the reaction was complex. As an example, III-1 on heating in a sealed tube at 95° for 24 h gave a 35% yield of trimethylsilyl ether and a 30% yield of dimethylmalonate. A fraction boiling at 120–150° 0.05 mm and some residue were also obtained.

ACKNOWLEDGEMENT

Support for this work by grants from the National Institutes of Health (Grant No. GM 16594) and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

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