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KETENE BIS(TRIALKYLSILYL) ACETALS: SYNTHESIS, PYROLYSIS AND SPECTRAL STUDIES

C. AINSWORTH* and YU-NENG KUO
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521 *(U.S.A.)*

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SUMMARY

Two high yield synthetic methods are described for the preparation of alkyl, dialkyl, aryl and diaryl ketene bis(trialkylsilyl)acetals. One is by reaction of α-metalated trimethylsilyl carboxylates with trimethylchlorosilane (TMCS) and the other is by interaction of dianions of carboxylic acids and TMCS. The dianion of cyclopropane carboxylic acid and TMCS gave *C*-silated ester in 90% yield. Pyrolysis of diphenyl ketene bis(trialkylsilyl) acetals to diphenyl ketene and bis(trialkylsilyl) ethers has been shown by crossover experiments to proceed intermolecularly. Pyrolysis of monosubstituted and dialkyl ketene bis(trimethylsilyl) acetals gave ketene–ketene acetal addition products (III) which on solvolysis afforded β-keto acids in high yield. NMR and mass spectral data are given for many of the compounds.

INTRODUCTION

Ketene acetals were extensively studied by McElvain[1] and in an accompanying paper we have recorded[2] a study of ketene alkyltrialkylsilyl acetals (I). This paper reports our findings in the area of ketene bis(trialkylsilyl) acetals (II). This type of compound has only recently been reported[3,4] and very little is known concerning its chemical reactivity.

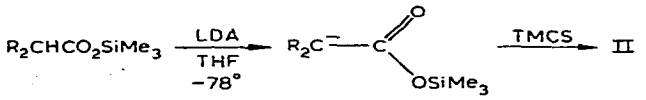
$R_2C{=}C(OR')OSiR'_3$ (I) $RR'C{=}C(OSiR''_3)_2$ (II)

RESULTS AND DISCUSSION

Synthesis of ketene bis(trialkylsilyl) acetals (II)

Two ways were developed for the synthesis of compounds (II). One procedure was analogous to the preparation of (I)[2]. Namely, the α-anion of trimethylsilyl carboxylates, prepared from the ester and the strong base lithium diisopropylamide (LDA) was treated in tetrahydrofuran (THF) with trimethylchlorosilane (TMCS).

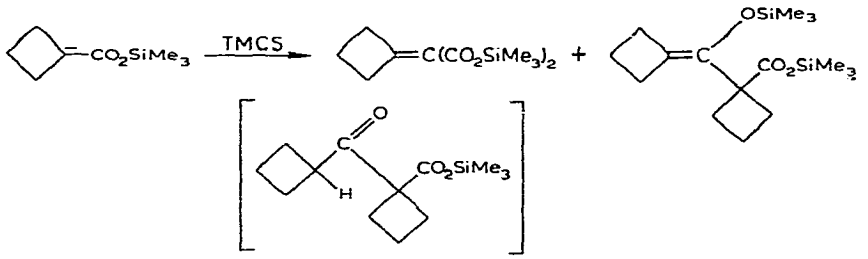
* Present address: Department of Chemistry, California State University at San Francisco, 1600 Holloway Avenue, San Francisco, California 94132 (U.S.A.).



The procedure was not always suitable for the synthesis of lower members of the series as it was accompanied by *C*-silation and condensation reaction. Metalated trimethylsilyl acetate and TMCS gave about equal amounts of *C*- and *O*-silation* whereas trimethylsilyl propionate gave only *O*-silated product. Metalated trimethyl-

$$C\bar{H}_2CO_2SiMe_3 \xrightarrow{TMCS} CH_2{=}C(OSiMe_3)_2 + Me_3SiCH_2CO_2SiMe_3$$

silylcyclopropane carboxylate gave a 10% yield of ketene acetal, a 40% yield of *C*-silated product and a 40% yield of condensation product. Trimethylsilylcyclobutane carboxylate, under similar conditions, gave ketene acetal and condensation product.

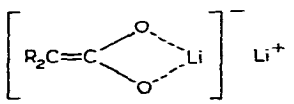


The condensation product that was isolated probably arose by reaction of ester with ester anion to form β-keto ester, followed by enolization and silylation. Interestingly, the same type of product (III) was obtained by the pyrolysis of dialkyl ketene bis-(trimethylsilyl) acetals (*vide infra*).

The other method of synthesis[4] involved treatment of the dianion of carboxylic acids with TMCS. The dianions were made from the acid and two equivalents of LDA[5].

$$R_2CHCO_2H \xrightarrow[0°]{LDA} R_2C^-CO_2^- \xrightarrow{TMCS} II$$

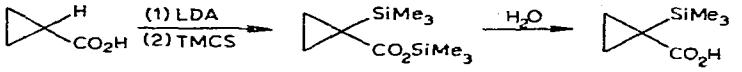
It was observed that phenyl and diphenyl acetic acids as dilithio salts are soluble in THF but the lithium carboxylates are insoluble. This observation may be explained by the increased solubility of the chelated lithium structure[5] shown below:



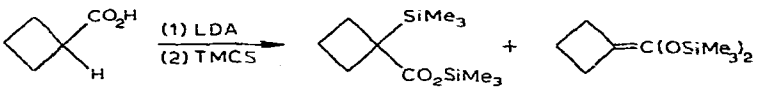
Ketene bis(trialkylsilyl) acetals were generally formed in high yield but acetic and propionic acid dianions and TMCS gave equal amounts of *C*- and *O*-silated products. t-Butyl acetic acid gave only ketene acetal, probably due to steric effects.

* Lutsenko and coworkers[3] have studied the rearrangement of ketene bis(trialkylsilyl) acetals to *C*-silated compounds.

The dianion of cyclopropanecarboxylic acid gave *C*-silated product only in 90% yield. Solvolysis of it to the corresponding carboxylic acid was quantitative.



Cyclobutane carboxylic acid in the reaction gave about equal amounts of *C*- and *O*-silated product.



Three synthetic procedures for the preparation of compounds (II) (Table 1) are briefly described below and are presented in detail in the Experimental section.

Method 1. The trimethylsilyl carboxylates were prepared in 80–85% yield from carboxylic acid and 10% excess sodium hydride followed by excess TMCS. The α-anion was formed at −78° using LDA in THF. TMCS was added and the product was obtained by distillation.

Method 2. The dianion of carboxylic acids was treated with TMCS at 0° followed by filtration and distillation to give ketene acetals (II), generally in 90–95% yield.

TABLE 1

KETENE BIS(TRIALKYLSILYL) ACETALS (II), $RR'C{=}C(OSiR''_3)_2$

Compound	*R*	*R'*	*R''*	*Yield*, (%)	*Method*[a]	*b.p.* (°C/*mm*)	*Formula*	*Analysis* (%)			
								Found		*Calcd.*	
								C	*H*	*C*	*H*
II-1[b]	H	H	Me	45, 45	1, 3[c]	50/15					
II-2	H	Me	Me	90, 60	1, 3	35/1.5	$C_9H_{22}O_2Si_2$	50.06	10.40	49.69	10.11
II-3	H	t-Bu	Me	90	3	42/0.5	$C_{12}H_{28}O_2Si_2$	55.61	11.10	55.32	10.83
II-4	Me	Me	Me	95	2	65/15	$C_{10}H_{24}O_2Si_2$	51.65	10.24	51.66	10.41
II-5	$-(CH_2)_2-$		Me	10, 0	1[d], 3	59/4.0	$C_{10}H_{22}O_2Si_2$				
II-6	$-(CH_2)_3-$		Me	40, 45	1, 3	50/0.3	$C_{11}H_{24}O_2Si_2$	54.25	9.77	54.07	9.90
II-7	$-(CH_2)_4-$		Me	95	2	60/0.1	$C_{12}H_{26}O_2Si_2$	55.92	10.16	55.75	10.14
II-8	$-(CH_2)_5-$		Me	95	2	95/0.4	$C_{13}H_{28}O_2Si_2$	57.90	10.52	57.29	10.35
II-9	H	Ph	Me	95	2	85/0.2	$C_{14}H_{24}O_2Si_2$	60.10	8.89	59.94	8.62
II-10	Me	Ph	Me	95	2	90/0.5	$C_{15}H_{26}O_2Si_2$	61.39	9.19	61.17	8.90
II-11	Ph	Ph	Me	95	2	120/0.1	$C_{20}H_{28}O_2Si_2$	67.31	7.95	67.36	7.91
II-12	Ph	Ph	Et	95	2	175/0.1	$C_{26}H_{40}O_2Si_2$	70.87	9.24	70.87	9.15
II-13	[e]		Me	95	2	150/0.1	$C_{20}H_{26}O_2Si_2$	67.72	7.44	67.76	7.39
II-14	[f]	[f]	Me	95	2	136/0.2	$C_{22}H_{32}O_2Si_2$	68.56	8.37	68.72	8.39

[a] See Experimental section.
[b] Reported[3].
[c] Both Methods 1 and 3 gave about an equal amount of *C*-silylated product. Slow addition of TMCS favored the acetal.
[d] Method 3 gave only *C*-silation in 90% yield and Method 1 gave *C*-silation in 40% yield and condensation product.
[e] 9-Fluorene.
[f] p-$CH_3(C_6H_4-)$.

Method 3. This method is like Method 2 except that the reaction was conducted at −78°.

All ketene bis(trialkylsilyl) acetals are sensitive to moisture, but they can be stored in sealed tubes at room temperature.

Pyrolysis of ketene bis(trialkylsilyl) acetals (II)

In an earlier publication we recorded[6] the pyrolysis study of ketene alkyltrialkylsilyl acetals (I).

Diphenyl ketene bis(trimethylsilyl) acetal (II-11) heated at 230° and 200 mm

TABLE 2

SPECTRAL DATA FOR COMPOUNDS (II), $RR'C{=}C(OSiR''_3)_2$

Compound	NMR data (CCl_4), δ values				IR C=C Stretch (cm^{-1})	UV (hexane)	
	$SiMe_3$	H	Me	Ph		λ_{max}	$\varepsilon \times 10^4$
II-1	0.20	3.1	—	—	—	—	—
II-2	0.16, 0.18	3.45	1.41	—	1680	—	—
II-3	0.18	3.42	1.01	—	1670	—	—
II-4	0.16	—	1.48	—	1700	—	—
II-5	0.19	[a]	—	—	1785	—	—
II-6	0.15	[b]	—	—	1724	—	—
II-7	0.15	[c]	—	—	1710	—	—
II-8	0.15	[d]	—	—	1690	—	—
II-9	0.25, 0.30	4.53	—	6.8–7.4 m	1640	266	1.64
II-10	0.01, 0.24	—	1.86	6.9–7.1 m	1660	262	0.83
II-11	0.00	—	—	7.19 s	1630	267	1.52
II-12	[e]	—	—	7.13 s	1630	—	—
II-13	0.34	—	—	[f]	1625	[g]	[g]
II-14	0.00	—	2.30	[h]	—	—	—

Mass spectral data, m/e (rel. intensity)

II-2 218(12) *M*, 147(95), 75(35), 73(100), 56(52), 45(31);
II-3 260(3) *M*, 245(21) *M*-15, 147(25), 83(100), 75(14), 73(43), 45(15);
II-4 232(8) *M*, 217(11) *M*-15, 147(36), 75(34), 73(100), 70(41), 55(27), 45(40);
II-6 244(5) *M*, 229(32) *M*-15, 147(100), 82(8), 75(26), 73(85), 54(9), 45(36);
II-7 258(4) *M*, 147(33), 96(11), 95(14), 75(46), 73(100), 68(25), 45(48), 41(25);
II-8 272(5) *M*, 185(11), 147(53), 110(8), 109(10), 83(17), 82(9), 81(25), 75(57), 73(100), 53(30), 45(44), 41(31);
II-9 280(10) *M*, 147(30), 118(92), 89(30), 75(20), 73(100), 45(49);
II-11 356(17) *M*, 194(33), 166(49), 165(27), 147(25), 75(15), 73(100), 45(34);
II-12 440(78) *M*, 297(9), 217(11), 194(25), 190(12), 189(20), 167(9), 166(17), 165(20), 161(9), 142(27), 115(31), 87(100), 59(77);
II-13 354(9) *M*, 192(47), 165(20), 164(29), 147(8), 75(10), 73(100), 45(25);
II-14 384(13) *M*, 222(20), 194(48), 179(26), 147(27), 75(15), 73(100), 45(35).

[a] 1.3–1.5 (m, 4).
[b] 1.7–2.1 (m, 2), 2.5 (t, 4).
[c] 1.4–1.8 (m, 4), 1.9–2.3 (m, 4).
[d] 1.1–1.6 (m, 6), 1.8–2.5 (m, 4).
[e] $SiEt_3$, 0.4–1.1 (m, 30).
[f] 7.1–7.4 (m, 4), 7.6–7.9 (m, 4).
[g] 237 (3.14), 280 (1.14), 321 (0.60), 336 (0.68).
[h] Aromatic protons 7.0 (d).

gave diphenyl ketene and bis(trimethylsilyl) ether*.

$$Ph_2C{=}C(OSiMe_3)_2 \xrightarrow{\Delta} Ph_2C{=}C{=}O + Me_3SiOSiMe_3$$

Diphenyl ketene bis(triethylsilyl) acetal (II-12) under the same conditions formed diphenyl ketene and a 30% yield of bis(triethylsilyl) ether**. Thermolysis of an equimolar mixture of II-11 and II-12 gave an ether fraction which in addition to the bis-ethers mentioned above also contained triethylsilyl trimethylsilyl ether***.

The crossover experiment result dictates that the reaction mechanism for the thermal cleavage of (II) is intermolecular, via free radical or heterolysis, in contrast with the intramolecular pathway established for the pyrolysis of (I)[6]. The difference in the pathways for systems (I) and (II) on thermolysis may be due to the greater steric factor in (II) that disfavors intramolecular reaction. Heating experiments of II-12 with 2,2'-azobis(2-methylpropionitrile) failed to initiate at a lower temperature, nor was there a change in product ratios, compared with control experiments†.

In addition to the 30% yield of bis(triethylsilyl) ether and some diphenyl ketene formed from the pyrolysis of II-12, interestingly, the major product, obtained in 60% yield, was triethylsilyl diphenylacetate. The formation of the latter compound may arise via a six-center reaction illustrated as follows:

Methylphenyl ketene bis(trimethylsilyl) acetals (II-10) behaved like II-12. Heated under reflux at atmospheric pressure for 15 hours, it gave a 50% yield of trimethylsilyl α-phenylpropionate††. The possibility of unsaturated silicon compounds by this type of reaction is under further study.

The pyrolysis of monoaryl, alkyl and dialkyl ketene bis(trimethylsilyl) acetals gave high yields of products called ketene–ketene acetal addition products. They are designated as compounds (III) and are described in Table 3. Their formation is consistent with a six-center reaction involving generated ketene and the starting ketene bis(trimethylsilyl)acetal†††. Steric factors should control the product so as to have the

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* Compound II-11 required a longer time and higher heating temperature than did the corresponding compound (I). Thus, the yield was reduced, being of the order of 50%, accompanied with ketene polymer.

** *Vide infra* for other products of the reaction.

*** The area/mol. wt. ratios of the gas chromatograph for the three silyl ether products were approximately 2.3/2.7/1.0 bis(trimethylsilyl) to triethylsilyl trimethylsilyl to bis(triethylsilyl) ethers. The theoretical value for these ratios, involving an intermolecular pathway, is complicated by the fact that II-12 is converted to diphenyl ketene and bis(triethylsilyl) ether in 30% yield only. Injection of a mixture of II-11 and II-12 into a gas chromatograph at 300° also gave the three ethers. A mixture of bis(trimethylsilyl) ether and bis(triethylsilyl) ether did not exchange under either thermolytic condition.

† No compounds arising from coupling products related to II-12 were observed in GLC product analysis. Thus, an ionic mechanism may best explain the crossover experiment results.

†† The methylphenylketene formed in the reaction polymerized.

††† This point was established by reaction of ketene and ketene bis(trimethylsilyl) acetal[8].

TABLE 3

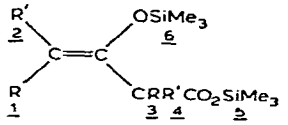
KETENE–KETENE ACETAL ADDITION COMPOUNDS (III), $RR'C{=}C(OSiMe_3)CRR'CO_2SiMe_3$

Compound	*R*	*R'*	*Yield* (%)	*b.p.* (°C/mm)	*Formula*	*Analysis* (%)			
						Found		*Calcd.*	
						C	*H*	*C*	*H*
III-1	H	Me	80	80/1.5	[a]	—	—	—	—
III-2	H	t-Bu	85	95/0.4	$C_{18}H_{38}O_3Si_2$	60.97	10.72	60.30	10.68
III-3	Me	Me	85–90	60/0.02	$C_{14}H_{30}O_3Si_2$	56.55	9.96	55.60	10.00
III-4	$-(CH_2)_4-$		85–90	135/0.6	$C_{18}H_{34}O_3Si_2$	60.72	9.42	60.99	9.67
III-5	$-(CH_2)_5-$		80	128/0.02	[a]	—	—	—	—
III-6	H	Ph	25	130/0.05	[a]	—	—	—	—

[a] Converted directly to β-keto acid.

TABLE 4

SPECTRAL DATA FOR COMPOUNDS (III),



Compound	*NMR shift* (CCl_4), δ *values at ambient temperature*						*IR* (cm^{-1})	
	1	2	3	4	5	6	*C=O*	*C=C*
III-1	4.56	1.50	2.92	1.18	0.22	0.15	1720	1680
III-2	4.72	1.07	2.75	1.02	0.25	0.25	1722	1660
III-3	1.58	1.50	1.24	1.24	0.25	0.19	1714	1664
III-4	1.5–2.4 (m, 16)				0.23	0.16	1712	1662
III-5	1.3–2.2 (m, 20)				0.23	0.16	1710	1640 br
III-6	5.44	7.2 (m)	4.28	7.3 (s)	0.25	0.02	1725	1655

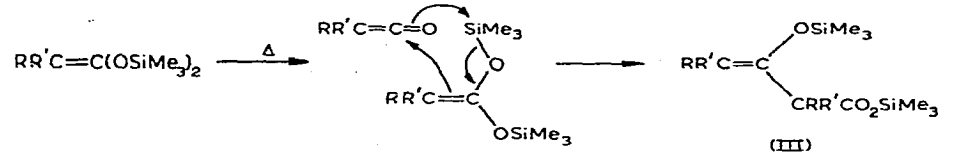
Mass spectral data, m/e (rel. intensity)

III-1 274(2) *M*, 259(24) *M*-15, 147(48), 83(15), 75(36), 73(100), 59(13), 56(7), 55(14), 45(35), 43(15);

III-2 358(3) *M*, 302(27), 288(19), 227(43), 215(18), 197(22), 171(35), 147(9), 130(33), 99(12), 83(29), 81(23), 75(40), 73(100), 57(75), 45(12), 44(36), 41(33);

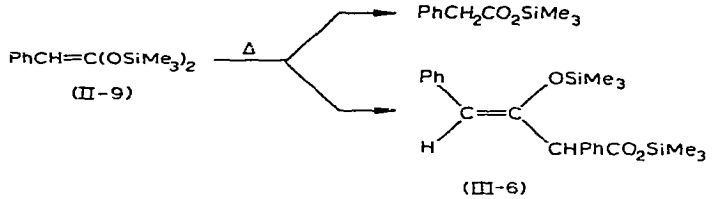
III-3 302(9) *M*, 287(29) *M*-15, 232(62), 217(25), 147(69), 95(26), 75(75), 73(100), 70(25), 57(15), 55(11), 45(15), 41(19);

III-6 398(4) *M*, 380(17), 280(22), 210(11), 192(9), 179(8), 147(15), 119(18), 118(26), 91(100), 75(14), 73(69), 65(14), 45(10).

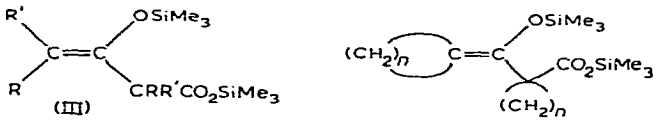


bulkier group, R or R', and the $OSiMe_3$ group *cis* about the ene system of (III).

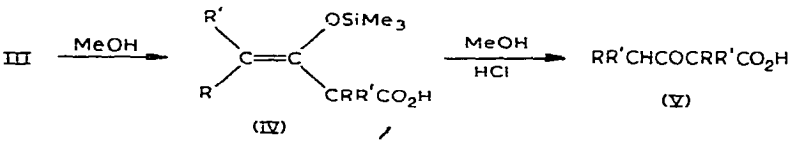
Heating of phenyl ketene bis(trimethylsilyl) acetal (II-9) in a sealed vessel at reflux formed two major products. One was trimethylsilyl phenylacetate* and the other was the ketene–ketene acetal addition product, III-6 (Table 3).



The alkyl and dialkyl compounds II-1 through II-8 (Table 1) on sealed tube thermolysis at high temperature for a long period gave the ketene–ketene acetal addition products (Table 3), represented below, in 85–90% yield.



These reaction products have an important utility. On solvolysis they are readily and quantitatively converted to highly substituted β-keto acids as is illustrated in the following equation.



As an example, III-2, R = H, R' = t-Bu, on standing at room temperature with methanol, gave IV-2 (Table 5). It solvolyzed at room temperature with methanol containing a catalytic amount of hydrochloric acid to give 2-t-butyl-3-oxo-5,5-dimethylhexanoic acid (V-2) (Table 6).

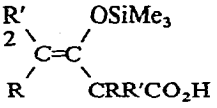
β-Keto acids are important biologically[9] and there are very few recorded examples of highly substituted β-keto acids**. The sequence of aliphatic carboxylic

* The formation of trimethylsilyl phenylacetate may involve a six-center reaction and the production of methylene dimethylsilane.

** α,α-Dimethyl acetoacetic acid, for example, has been employed in the synthesis[10].

TABLE 5

SPECTRAL DATA FOR 3-TRIMETHYLSILYLOXY 3-ALKENOIC ACIDS (IV),



Compound	R	R'	NMR shift (CCl_4), δ value at ambient temperature				
			$SiMe_3$	1	2	3	4
IV-1	H	Me	0.16	4.56(q)	1.5(q)	2.92(q)	1.18(d)
IV-2[a]	H	t-Bu	0.25	4.72	1.07	2.72	1.02
IV-3	Me	Me	0.23	1.62	1.54	1.33(s)	1.33(s)
IV-4	$-(CH_2)_4-$		0.23	[b]	—	—	—
IV-5	$-(CH_2)_5-$		0.23	[c]	—	—	—
IV-6	H	Ph	0.02	5.44	7.2(m)	4.28(s)	7.3(s)

Mass spectrum

IV-2 *m/e* (rel intensity) 286(12) *M*, 242(13) *M*-44, 227(100), 171(73), 130(67), 99(19), 83(11), 81(34), 75(27), 73(67), 57(73), 44(17), 41(20).

[a] Obtained as a solid, m.p. 82°. Anal.: Found: C, 63.19; H, 10.50. $C_{15}H_{30}O_3Si$ calcd.: C, 62.90; H, 10.56%.
[b] 1.5–2.4 (m, 16).
[c] 1.3–2.2 (m, 20).

TABLE 6

SPECTRAL DATA OF β-KETO ACIDS (V), $RR'CHCOCRR'CO_2H$ (1 2 3 4)

Compound	R	R'	m.p. (°C/mm)	NMR shift (CCl_4), δ value at ambient temperature			
				1	2	3	4
V-1	H	H	liq.	1.06 (t, 3)	2.53 (q, 2)	3.42 (q, 1)	1.33 (d, 3)
V-2[a]	H	t-Bu	78	1.02 (s, 9)	2.42 (s, 2)	3.30 (s, 1)	1.10 (s, 9)
V-3	Me	Me	24	1.12 (d, 6)	2.96 (m, 1)	1.40	1.40
V-4	$-(CH_2)_4-$		62	[b]	—	—	—
V-5	$-(CH_2)_5-$		142	[c]	—	—	—
V-6	H	Ph	[d]	3.62	7.3	4.62	6.9–7.3

Mass spectrum

V-2 *m/e* (rel intensity) 214(0.3) *M*, 170(12) *M*-44, 99(78), 71(11), 58(9), 57(100), 44(12), 41(15).

[a] Anal.: Found: C, 67.30; H, 10.23. $C_{12}H_{22}O_3$ calcd.: C, 67.26; H, 10.35%.
[b] 1.4–2.3 (m, 15) and 1.4–2.7 (m, 1).
[c] 1.3–2.2 (m, 19) and 2.3–2.6 (m, 1).
[d] Not determined.

acid to ketene bis(trimethylsilyl) acetal followed by thermolysis and solvolysis afforded the β-keto acids of Table 6 in 75–80% overall yield. However, a more practical synthesis of β-keto acids has been developed from the reaction of the dianion of carboxylic acids and esters[11]. In this method, the product is best obtained via the trimethylsilyl ester. Reaction involving the dianion of isobutyric acid is illustrated below.

$$Me_2C^-CO_2^- + R'CO_2Me \rightarrow R'COCMe_2CO_2^- \xrightarrow{TMCS}$$

$$R'COCMe_2CO_2SiMe_3 \xrightarrow{MeOH} R'COCMe_2CO_2H$$

Spectroscopic studies

NMR, IR, and UV studies. The spectral data for compounds (II) are shown in Table 2. In essence, the NMR data of compounds (II) are in agreement with the analysis of the data for compounds (I)[2,12]. Thus, II-11, R = R' = Ph, shows the $SiMe_3$ signal at that of TMS, whereas the fluorenyl compound II-13 shows it at lower field by 20 Hz. This is consistent with the phenyls of II-11 being non-coplanar with the ene system and having the methyl protons of $SiMe_3$ in the positive shielding cone of the phenyl ring. This condition is restricted in II-13.

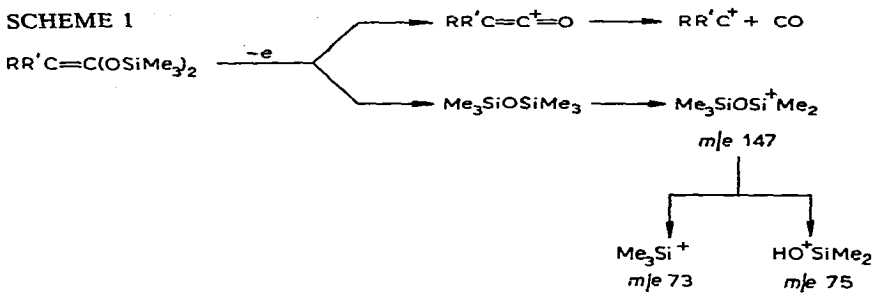
It is also noted that the IR C=C stretch frequency of II-11 at 1630 cm^{-1} is not indicative of much conjugation, and the extinction coefficient value for the UV spectrum does not indicate a high degree of conjugation. Indeed, based on analogy with diphenyl ketene methyl trimethylsilyl acetal, it seems likely that at room temperature, freedom of rotation exists about the double bond of II-11 and a large contributor to the structure is the polar one, $Ph_2C^- - C^+(OSiMe_3)_2$.

The NMR spectrum of compound II-10, R = Me, R' = Ph, at room temperature shows two $SiMe_3$ signals, one at that of TMS and the other at 14 Hz downfield. Our assignment for the higher $SiMe_3$ signal is that of a *cis*-arrangement of it with respect to phenyl, on the assumption that the phenyl group is non-coplanar and the $SiMe_3$ group is influenced by the positive shielding zone of the phenyl ring. In contrast, the NMR spectrum of II-9, R = H, R' = Ph, shows both $SiMe_3$ signals relatively downfield and the UV extinction coefficient relatively large compared with that of II-10, consistent with a coplanar arrangement of the phenyl group and the ene system. The NMR $SiMe_3$ signals for compounds II-1 through II-4 are of interest regarding the coincidental shift values for the unsymmetrical compound II-3.

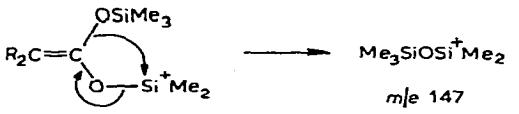
The stereochemical factors relate to the formation of compound III-6 (*vide ultra*) which should result in a *cis*-arrangement of the phenyl and $OSiMe_3$ groups attached to the ene system. Based on analogy with II-9, this phenyl should be coplanar with the ene system, having its NMR signal appearing as a multiplet[2]. The $SiMe_3$ signal (see column 6, Table 4) should be in the δ 0.15–0.20 range. However, it is near the value of TMS. This phenomenon is similar to that observed for the ketene–ketene acetal addition compound from phenyl ketene methyltrimethylsilyl acetal[2]. Perhaps the $SiMe_3$ protons attached to the ene system are time averaging in the positive shielding region of the phenyl of the $CHPhCO_2SiMe_3$ moiety. A similar effect was observed for compound IV-6(Table 5). It is of interest to note the odd coincidence of $SiMe_3$ coalescence in II-2 and II-3.

Mass spectral studies. The mass spectral fragmentation for compounds II (Table 2) follows the pattern shown in Scheme 1. The base peak is often *m/e* 73 or

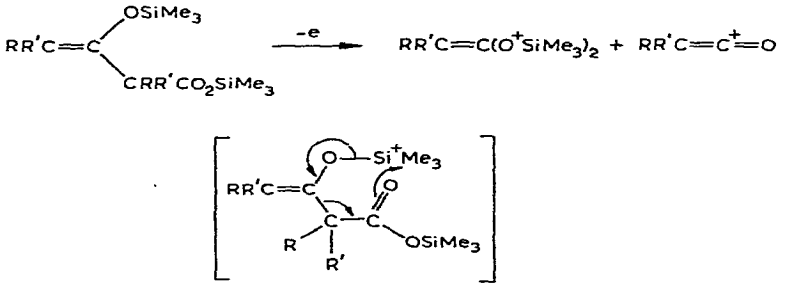
SCHEME 1



the ketene peak. The *m/e* 147 peak is always present and is the base peak in II-6. The formation of *m/e* 147 is probably via intramolecular reaction[13,14] in the fashion shown below. The *m/e* 147 peak has a very low value in the spectrum of the fluorenyl compound II-13. The difference between compounds II and I on mass spectral analysis is the presence of a strong *m/e* 89 peak for the latter.

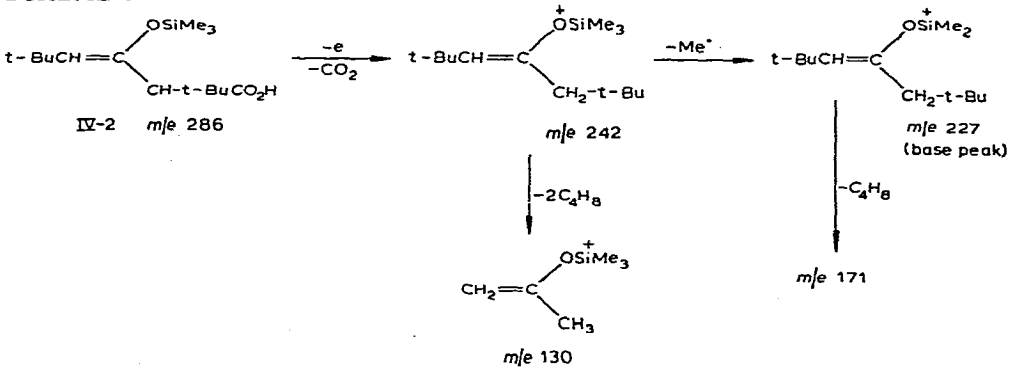


The mass spectral fragmentation of compounds III (Table 4) resulted in a reversal of their formation from ketene and ketene bis(trialkylsilyl) acetal.



Compound IV-2 (Table 5) on electron bombardment probably fragmented

SCHEME 2



via loss of CO_2 to give an acrylic trimethylsilyl enol ether ion. This *m/e* 242 species gave stable fragments *m/e* 227, by loss of CH_3 from the trimethylsilyl moiety, and *m/e* 130 via loss of two isobutylenes as shown in Scheme 2[15].

The mass spectrum of the β-keto acid V-2, (Table 6) with parent ion *m/e* 214, underwent loss of carbon dioxide to give the dineopentyl ketone ion *m/e* 170 which gave daughter fragments t-Bu$CH_2\overset{+}{C}O$ *m/e* 99, t-Bu$\overset{+}{C}H_2$ *m/e* 71, and t-$B\overset{+}{u}$ *m/e* 57.

EXPERIMENTAL

M.p's. were taken with a Fisher–Johns m.p. apparatus, b.p's. are uncorrected. NMR studies were done using a Varian A60A spectrometer; infrared spectra were taken on a Perkin–Elmer Model 457 spectrophotometer; ultraviolet measurements were made on a Perkin–Elmer Model 402 spectrophotometer and mass spectra were measured with an AEI Model MS12 spectrometer at an ionization voltage 70 eV, 100 μamp trap current, source temperature 150–200°, and source pressure 0.5–1.0 ($\times 10^{-6}$) mm. Microanalyses were done by Midwest Microlab Ltd., Indianapolis, Indiana (U.S.A.).

Preparation of starting trialkylsilyl esters

Sodium hydride (52% oil dispersion, 5.1 g (0.12 mole)) was washed twice by decantation using 25 ml portions of anhydrous ether to remove the oil. To a suspension of the washed sodium hydride in 200 ml of anhydrous ether was added, with stirring, 0.1 mole of carboxylic acid dissolved in 50 ml of dry ether. Addition rate was such that the mixture maintained reflux. Trialkylsilyl chloride (0.15 mole) was added slowly and the mixture was heated under reflux for 1-2 h. The mixture was filtered or centrifuged and the solution was concentrated by careful heating (lower molecular weight esters boiled below steam bath temperature). The residue was distilled to give trialkylsilyl ester. The following compounds were prepared in about 80% yield using the above procedure:

1. *Trimethylsilyl acetate*, b.p. 95° [lit.[16] b.p. 102°]; NMR (CCl_4) δ 0.21 (s, 9), and 1.98 ppm (s, 3).

2. *Trimethylsilyl propionate*, b.p. 115° [lit.[16] b.p. 122°]; NMR (CCl_4) δ 0.20 (s, 9), 1.04 (t, 3), and 2.2 ppm (q, 2).

3. *Trimethylsilyl isobutyrate*, b.p. 130°; NMR (CCl_4) δ 0.23 (s, 9), 1.07 (d, 6), and 2.43 ppm (m, 1); mass spectrum *m/e* (rel. intensity) 160(1) *M*, 147(11), 145(42), 75(87), 73(100), 45(22), 43(26) 41(11).

4. *Trimethylsilyl cyclopropanecarboxylate*, b.p. 149°; NMR (CCl_4) δ 0.7–1.1 (m, 4), and 1.4–1.7 ppm (m, 1); mass spectrum *m/e* (rel. intensity) 158(0) *M*, 143(99) *M*-15, 99(28), 75(100), 73(45), 69(19), 59(14), 47(16), 45(46), 43(20), 41(43), 39(40).

Anal. Found: C, 53.59; H, 8.82. $C_7H_{14}O_2Si$ calcd.: C, 53.12; H, 8.92%.

5. *Trimethylsilyl cyclobutanecarboxylate*, b.p. 65°/15 mm; NMR (CCl_4) δ 0.23 (s, 9), 1.9–2.5 (m, 6), and 3.02 ppm (m, 1); IR (neat) 2970, 1715, 1360, 1258, 1195, 1058, 850, 768, and 732 cm^{-1}; mass spectrum *m/e* (rel. intensity) 172(2) *M*, 157(65), 129(16), 75(81), 73(100), 55(20), 45(16).

Anal. Found: C, 55.98; H, 9.41. $C_8H_{16}O_2Si$ calcd.: C, 55.79; H, 9.36%.

6. *Trimethylsilyl phenylacetate*, b.p. 95°/2.5 mm; NMR (CCl_4) δ 0.21 (s, 9), 3.49 (s, 2), and 7.2 ppm (s, 5); mass spectrum *m/e* (rel. intensity) 208(1) *M*, 193(10), 164(14), 91(21), 75(35), 73(100), 65(14), 45(20).

Anal. Found: C, 63.72; H, 7.70. $C_{11}H_{16}O_2Si$ calcd.: C, 63.44; H, 7.74%.

7. *Trimethylsilyl diphenylacetate*, b.p. 125°/1 mm; NMR ($CDCl_3$) δ 0.24 (s, 9), 5.02 (s, 1), and 7.32 ppm (s, 10); mass spectrum *m/e* (rel. intensity) 284(0) *M*, 269(3.5) *M*-15, 240(12), 167(11), 165(18), 75(13), 73(100).

Anal. Found: C, 71.53; H, 7.10. $C_{17}H_{20}O_2Si$ calcd.: C, 71.81; H, 7.09%.

8. *Triethylsilyl diphenylacetate*, b.p. 165°/0.5 mm; NMR (CCl_4)δ 0.5–1.1 (m, 15), 4.81 (s, 1), and 7.22 ppm (s, 10); IR (neat) 3040, 2970, 1500, 1200, 750, and 700 cm^{-1}.

Anal. Found: C, 73.38; H, 8.22. $C_{20}H_{26}O_2Si$ calcd.: C, 73.59; H, 8.03%.

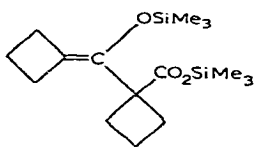
Preparation of lithium diisopropylamide (LDA)[5]

To a 250 ml oven-dried 3-neck flask equipped with a magnetic stirrer and addition funnel was added a solution of 10 g (0.1 mole) of diisopropylamine and 75 ml of dry THF and the system was swept with dry N_2 and cooled in an ice bath. A hexane solution of 50 ml of 2 *M* (0.1 mole) n-butyllithium was added over a 5 min period and the solution was stirred for an additional 15 min.

Synthesis of ketene bis(trialkylsilyl) acetals (II), $RR'C{=}C(OSiR''_3)_2$

Method 1. Lithium diisopropylamide (0.05 mole) was cooled to −78° and 0.05 mole of trimethylsilyl ester dissolved in 20 ml of THF was added. After stirring for 30 min, 25 ml (0.25 mole) of TMCS was added over a 5 min period. The reaction mixture was allowed to warm to room temperature during a stirring period of 30 min. The mixture was filtered quickly and the solvent was removed using a rotary evaporator. The residue was treated with 25 ml of dry ether and the mixture was refiltered. The ether was removed by evaporation and the residue was distilled under reduced pressure. Compounds prepared by this method are listed in Table 1.

Trimethylsilylcyclobutane carboxylate gave a 40% yield of II-6 and a 15% yield of:



b.p. 92°/0.2 mm. Anal. Found: C, 59.50; H, 9.36. $C_{16}H_{30}O_3Si_2$ calcd.: C, 58.87; H, 9.26%.

Method 2. To lithium diisopropylamide (0.1 mole) was added dropwise a solution of 0.05 mole of carboxylic acid in 25 ml of THF. Temperature was maintained near 0° and stirring was continued for 30 min. An excess of TMCS* (25 ml, 0.25 mole) was added over a 5 min period and the mixture was allowed to warm to room temperature while being stirred for 30 min. The mixture was quickly filtered and the filtrate was concentrated using a rotary evaporator. About 20 ml of dry ether was added and the mixture was refiltered. The ether was removed by evaporation and the residue was distilled under reduced pressure. The products obtained are listed in Table 1.

Method 3. This procedure is essentially the same as Method 2 except the reaction temperature was held at −78° using Dry-ice–Acetone cooling. Following addi-

* Triethylchlorosilane was substituted for TMCS for the preparation of II-12.

tion of TMCS, the mixture was allowed to warm to room temperature and worked up according to Method 2.

Pyrolysis of compounds (II), $RR'C{=}C(OSiMe_3)_2$

1. *Pyrolysis of alkyl ketene trialkylsilyl acetals.* As a general procedure, 0.05 mole of alkyl ketene bis(trimethylsilyl) acetal was sealed in a 15 ml Pyrex tube and immersed in an oil bath at 230–240° for three days. The tube was cooled to −78° and opened. The residue was distilled and gave bis(trimethylsilyl) ether (90% yield) and ketene–ketene acetal addition products (III) in about 85% yield. The following compounds were pyrolyzed according to this procedure and the products (III) are described in Table 3.

Compound	*Ketene–ketene acetal adduct*
II-2	III-1
II-3	III-2
II-4	III-3
II-7	III-4
II-8	III-5

2. *Pyrolysis of monoaryl ketene bis(trialkylsilyl) acetals.* Compounds II-9 and II-10, heated in sealed tubes at 220° for 4 h, gave the same results as when heated at atmospheric pressure.

(a) Compound II-9 (7.1 g, 0.025 mole) was heated under reflux for 2 h. The product was distilled and gave 3 g of trimethylsilyl phenylacetate and 2 g of ketene–ketene acetal addition compound III-6 (Table 3).

(b) Compound II-10 (7.5 g, 0.025 mole) was heated under reflux for 15 h. The product was distilled under reduced pressure and gave 1 g of bis(trimethylsilyl) ether and 2.8 g of trimethylsilyl α-phenylpropionate: b.p. 90°/2 mm; NMR (CCl_4) δ 0.21 (s, 9), 1.5 (d, 3), 3.65 (q, 1), and 7.3 ppm (s, 5).

3. *Pyrolysis of diaryl ketene bis(trialkylsilyl) acetals.* As general procedure, 0.05 mole of diaryl ketene bis(trialkylsilyl) acetal was heated at 230° under 200 mm pressure for 1 h. During this period bis(trialkylsilyl) ether was collected. The residue was distilled under reduced pressure to give product.

(a) Compound II-11 gave diphenyl ketene (50%) and bis(trimethylsilyl) ether (85% yield): b.p. 95°; NMR (CCl_4) δ 0.04 ppm; mass spectrum *m/e* (rel. intensity) 162(0) *M*, 147(100) *M*-15, 73(27), 59(13), 45(16).

(b) Compound II-12 gave bis(triethylsilyl) ether (30% yield) and a 10% yield of diphenyl ketene. The major product, in 60% yield, was triethylsilyl diphenylacetate. Bis(triethylsilyl) ether: b.p. 82°/1 mm; NMR (CCl_4) δ 0.3–0.7 (m, 12), and 0.8–1.2 ppm (m, 18); mass spectrum *m/e* (rel. intensity) 246(1) *M*, 217(100) *M*-29, 189(57), 165(22), 161(31), 133(11), 131(7), 105(16), 103(11), 94(10), 80(15), 66(15), 59(13).

(c) Pyrolysis of II-11 and II-12. A mixture of equimolar quantities of II-11 and II-12 gave diphenyl ketene, triethylsilyl diphenylacetate and an ether fraction. The ether fraction was distilled and the middle boiling fraction was the unsymmetrical ether. Triethylsilyl trimethylsilyl ether: b.p. 125°; NMR (CCl_4) δ 0.04 (s, 9), 0.3–0.7

(m, 6), and 0.8–1.2 ppm (m, 9); mass spectrum *m/e* (rel. intensity) 204(1) *M*, 175(88), 147(100), 119(39).

The crude ether fraction, analyzed by GLC, was shown by comparison with authentic samples to contain bis(trimethylsilyl) ether, trimethylsilyl triethylsilyl ether and bis(triethylsilyl) ether. Equimolar quantities of II-11 and II-12 were injected into a GLC Carbowax column at an injection temperature of 300° and the ether fraction contained the above three ethers.

Solvolysis of silyl compounds

1. *Solvolysis of (II), $RR'C{=}C(OSiR''_3)_2$.* As an example, a solution of 0.01 mole of II-11 and 0.01 mole of methanol in 20 ml of carbon tetrachloride was allowed to stand at room temperature for 30 min. The solvent was evaporated and trimethylsilyl diphenylacetate was obtained in near quantitative conversion. When excess methanol was used, diphenylacetic acid was obtained in quantitative yield.

2. *Solvolysis of trimethylsilyl α-trimethylsilylcyclopropane carboxylate.* Trimethylsilyl α-trimethylsilylcyclopropane carboxylate (b.p. 45°/0.2 mm) was stood in methanol for 10 min. The solvent was evaporated and the residue was pure α-trimethylsilylcyclopropane carboxylic acid: m.p. 106°; NMR (CCl_4) δ 0.06 (s, 9), 0.72 (t, 2), 1.15 (t, 2), and 12.1 ppm (s, 1); IR (Nujol) 3100–2500, 1738, 1300, 1250, 950 and 848 cm^{-1}.

Anal. Found: C, 53.14; H, 8.91. $C_7H_{14}O_2Si$ calcd.: C, 53.12; H, 8.92%.

3. *Solvolysis of (III), $RR'C{=}C(OSiMe_3)CRR'CO_2SiMe_3$.* (a) Equimolar quantities of compound (III) and methanol in carbon tetrachloride were allowed to stand at room temperature for 30 min. The solvent was removed using a rotary evaporator and the resulting solid was recrystallized from petroleum ether by cooling to −78°. The silyl ethers (IV) that formed are given in Table 5.

(b) About 1 g of compound (III) and 2 ml of methanol containing 1% concentrated hydrochloric acid was allowed to stand at 0° for 30 min. The excess methanol was removed using a vacuum pump and the resulting solid was recrystallized from petroleum ether (b.p. 50°). The β-keto acids (V) that formed are described in Table 6.

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