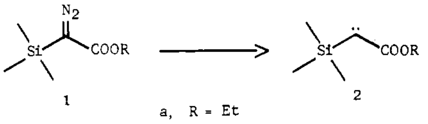
Photochemical Decomposition of Trimethylsilyl Diazoacetates in Alcohols[1,2]

Wataru Ando,*[3a] Akira Sekiguchi,[3a] Tsuneo Hagiwara,[3b] Toshihiko Migita,[3b] Vinay Chowdhry,[3c] F. H. Westheimer,*[3c] Seetha L. Kammula,[3d] Marilyn Green,[3d] and Maitland Jones, Jr.*[3d]

Contribution from the Departments of Chemistry, University of Tsukuba, Ibaraki, 300-31, Japan, Gunma University, Kiryu, Gunma, Japan, Harvard University, Cambridge, Massachusetts 02136, and Princeton University, Princeton, New Jersey 08544. *Received March 12, 1979*

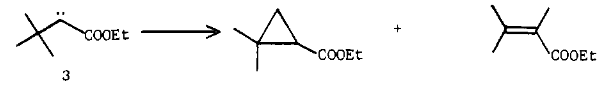
Abstract: Photolysis of trimethylsilylcarboalkoxy diazoacetates in alcohols yields the products of insertion of the corresponding carbenes into the O-H bond, compounds derived from Wolff rearrangement, and the compounds most simply attributed to trapping of silenes. However, in the gas phase the immediate precursor to this third type of compound is not the silene but rather a dimethylalkoxysilylketene. The source of this ketene is discussed. Dimethylphenylsilylcarboalkoxycarbene is shown to yield a similar ketene very efficiently. Reactions of trimethylsilylcarbene and of phenyltrimethylsilylcarbene in alcohols are also described.

Intramolecular reactions of carbenes are attractive as potential sources of unstable molecules in general[4] and of silenes[5] in particular. Thus both intramolecular carbon-hydrogen insertion leading to cyclopropanes and carbon-carbon insertion to give alkenes are well precedented,[6] and one might expect silicon-containing carbenes to behave similarly to give siliranes and silenes.[6] We report here the details of our studies of the reactions of carbenes **2a** and **2b** derived from the trimethylsilyl diazoacetates **1a** and **1b**. In particular, we describe the photolysis and thermolysis of the silyldiazo esters, **1a** and **1b.** Some of the reactions they undergo, although conveniently discussed in terms of the carbenes **2a** and **2b**, may prove to be concerted.[7]

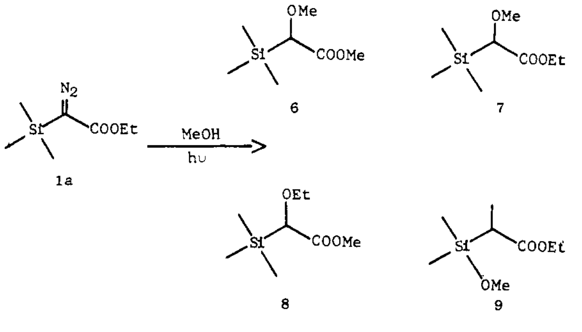

1 2

a, R = Et
b, R = Me

The analogous all-carbon carbene **3** gives cyclopropane **4** and acrylate **5** in the ratio 35/65.[8] Although this result is suggestive, the notorious instability of silenes[5] makes it unlikely that the silicon-containing analogue of **5** would be stable. Therefore, it was decided to take advantage of the rapid reaction of silenes with alcohols[5] and to attempt to isolate stable alkoxysilanes. Thus we began with the photochemical decomposition of **1a** in methanol. Four major products were isolated in ca. 90% yield. Table I gives the relative yields under different irradiation conditions.

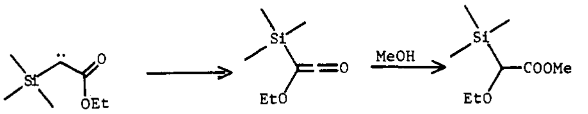

3 4 5

Ester **7** definitely seems a product of the direct reaction of carbene **2a** with methanol.[8] Although its high yield is in accord with the proposed structure, and the spectra are reasonable for **7**, there is a problem in differentiating **7** from the minor product **8** in which the positions of the ethoxy and methoxy groups are interchanged. Synthesis of **7**-d_4 and **8**-d_4 by reaction of **2a** with perdeuteriomethanol simplified the ^{1}H NMR spectra and provided further information supporting the assignment of structure. In **8**-d_4 the diastereotopic methylene protons of the -OC$_2$H$_5$ group give rise to a pair of multiplets (eight lines each would be expected). The signal from the corresponding methyl group apears as a triplet because the coupling constants between it and the two methylene protons are fortuitously equivalent. Similar spectra from diastereotopic protons have previously been observed.[9] In the present case decoupling of the methyl protons reduces the multiplets from the methylene group to a pair of doublets and irradiation of one of the methylene signals causes the methyl signal to collapse to a doublet. In **7**-d_4 the methylene protons give rise to a quartet, presumably because of their greater distance from the center of asymmetry in the molecule.

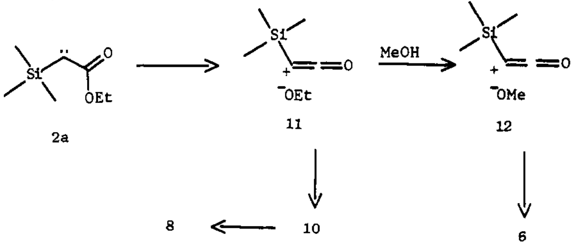


1a 6 7 8 9

No similar ambiguity exists for **6**, which could readily be identified through an examination of its spectra. Compounds **6** and **8** owe their formation to a Wolff rearrangement. Direct Wolff rearrangement leads to a ketene **10** that can give **8** by methanolysis. However, Wolff rearrangements of alkoxy groups have been postulated to involve ionic components,[10] and the ion pair **11** can either collapse to **10** or exchange with solvent to give a new ion pair **12** as the source of **6.**



2a 10 8



2a 11 12 10 6 8

Most interesting of all the products is **9**, for the most logical precursor to it is the silene **13** formed by methyl migration in **2a.**

The reaction is general, as photolysis of **1a** in ethanol, isopropyl alcohol, or *tert*-butyl alcohol gives similar products. The

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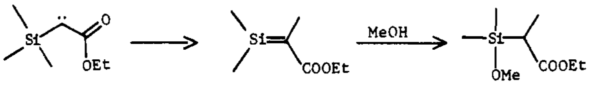
Table I. Irradiation of **1a** in Methanol

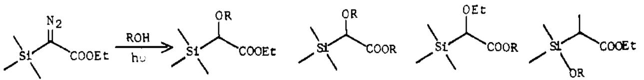
conditions	6	7	8	9	X[d]
$h\nu^a$	12	64	14	10	
$h\nu^b$	9	49	24	13	5
$h\nu^c$	*e*	70	*e*	~3-4	
$h\nu^a$ + LiCl	12	56	23	9	
$h\nu^a$ + LiBr	10	51	20	19	

[a] Rikosha 400-W high-pressure mercury lamp, through Pyrex for 5 h, with 1.1 M solutions. [b] Rayonet RPR 100 reactor, with 16 2537-Å lamps, through quartz for 1.5 h, with 0.5-0.6 M solutions. [c] Same as above, with 3500-Å lamps. [d] Structure unknown. [e] Not quantified.



2a **13** **9**

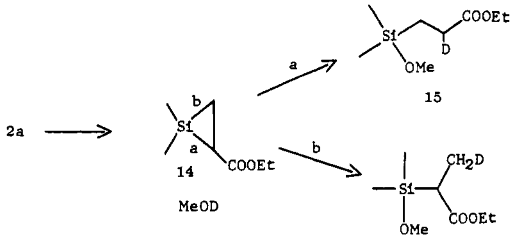
relative difficulty in forming insertion product and the concomitant increase in apparent methyl migration may reflect an increased steric barrier to insertion, leaving the way open for other reactions to dominate.



R = Et		87		13
R = i-Pr	35	22	22	21
R = t-Bu	40	8	17	35

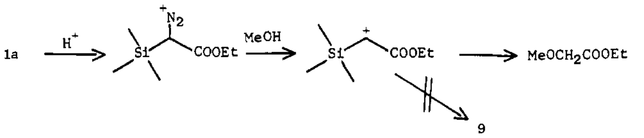
Although compound **9** is logically attributed to reaction of silene **13**, there are other mechanistic possibilities and the bulk of the remainder of this paper will be devoted to an analysis of them.

First of all, silirane **14** is not a source of **9**. Were **14** to be formed, it would surely react with methanol-*O-d*,[11] but the expected methanolysis product would be **15**, not **9**, since bond "a" is more likely to break than bond "b". But even if the "wrong" bond were cleaved on methanolysis, the product would be deuterated in the aliphatic methyl group, which it is not.

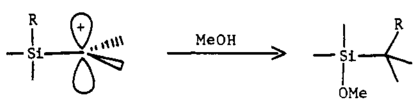


14 **15** **9**

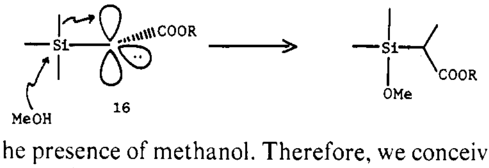
An ionic mechanism can be written for the formation of **9**, and such processes have previously been postulated to occur when diazo compounds are decomposed in alcohols.[12] However, treatment of **1a** with methanolic HCl or the thermal decomposition of **1a** in methanol led only to ethyl methoxyacetate and not to **9**. Further evidence against the formation of such ions comes from the irradiation of **1a** in a methanol solution of LiBr or LiCl. The product ratio was little affected (see Table I).



A third mechanistic possibility is much more difficult to dismiss. Generation of a positive center α to a trialkylsilyl



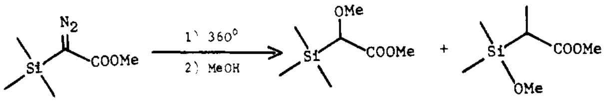
group is known to induce migration from silicon to carbon,[13] with a nucleophile simultaneously or subsequently attaching to silicon. Although the multiplicity of trimethylsilylcarboethoxycarbene is at present unknown, it may prove to have the structure of the singlet, **16**. Might a carbonium ion process take place in the carbene **2a**? That is, might a mechanism occur in which alkyl migration toward the empty p orbital of the carbene is accompanied by, or preceded by, attack by solvent methanol on silicon (eq 1)? Both of these possibilities depend



16 (1)

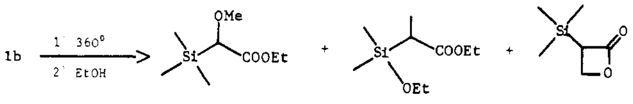
on the presence of methanol. Therefore, we conceived the idea of generating **2a** in the gas phase and adding methanol later. The absence of **9** would be evidence for a mechanism bypassing **13**, whereas the continued formation of **9** would be consistent with the intervention of the silene.

Methyl trimethylsilyldiazoacetate (**1b**) was evaporated through a Pyrex tube maintained at 360 °C and the products were washed off a cold finger with excess methanol. Gas chromatography on a ¼ in. × 2 m 10% Carbowax 20M on Chromosorb W column at 120 °C revealed two major products, **6** and methyl α-dimethylmethoxysilylpropionate (**17b**).



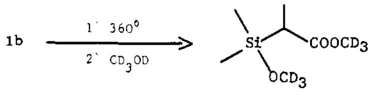
1b **6** **17b**

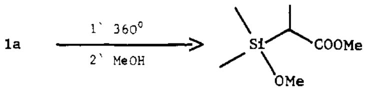
Ostensibly the case for silene **13** would seem fairly sound. However, further observations cloud the picture. Thus diazoacetate **1b** was evaporated through an empty Pyrex tube held at 360 °C into a trap cooled to −78 °C to which *ethanol* was added. The major product was that formed by Wolff rearrangement and capture (**7**), but the product of rearrangement and alcohol capture, **17a**, was also found in 9% yield. Notice that *both* alkoxy groups are ethoxy. There was in addition a new compound **18** formed in 4% yield. Analysis of the spectra



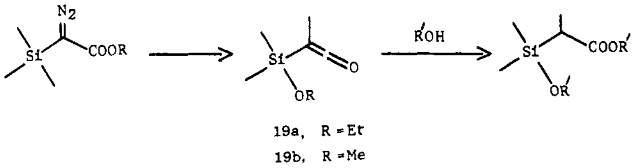
7 **17a** **18**

revealed **18** to be a β-lactone, doubtless produced by intramolecular insertion into the proximate carbon-hydrogen bond. Although β-lactones have not been isolated previously from carbenes, they have been postulated,[14] and larger ring lactones have been found in related reactions.[15] Similarly, gas-phase generation of **2b** followed by trapping with tetradeuteriomethanol or pyrolysis of **1a** followed by trapping with methanol revealed that *both* alkoxy groups in **9** are derived

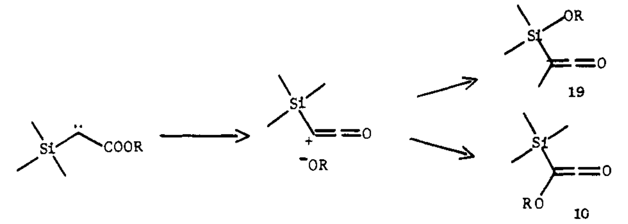


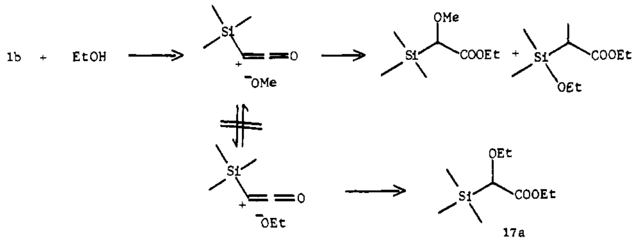


from the *added* alcohol! This observation led us to attempt the isolation of ketene **19**, the suspected intermediate. When the pyrolysate of **1a** or **1b** was collected into a trap containing dry benzene at −78 °C, ketenes **19a** or **19b** could be isolated in 5–11% yield. Moreover, when treated with alcohols, **19** gave the twice-exchanged esters in quantitative yield! Thus the immediate source of **9** is not the silene, but ketene **19**. Of course this result holds strictly only for the gas-phase experiments, and ketene **19** cannot be involved in solution, as **9** contains two *different* alkoxy groups. Either the silene or the "direct" mechanism of eq 1 must apply in solution.

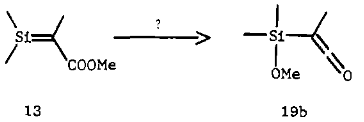


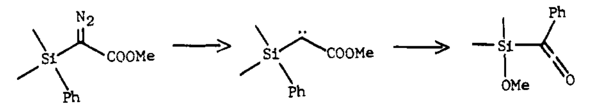
A major question still remains as to the source of **19**. The gas-phase Wolff rearrangement may have a radical or even ionic component. As an alkoxy group migrates to an adjacent position on its way to ketene **10**, it finds itself in the neighborhood of a silicon atom and adds with or without simultaneous migration of a methyl group. No escape from the ion or radical pair can occur, however, as copyrolysis of methyl trimethylsilyldiazoacetate (**1b**) with ethanol in a nitrogen-flowing system gave *no* exchanged Wolff product, **17a**.





Another important mechanistic possibility involves isomerization of the silene to the rearranged ketene **19**. If this mechanism applies, the rearrangement must be very fast indeed. We anticipated that phenyl migration in carbene **20** might be more efficient than the previously discovered methyl shifts and this proved to be the case, as ketene **21** could be isolated in 51% yield. Even in this relatively facile reaction attempts to trap a silene were in vain. Silenes are known[16] to react efficiently with aldehydes to give alkenes in a Wittig-type reaction. Yet generation of **20** in the presence of benzaldehyde led to no **22**; ketene **21** was isolated instead. Similar results were obtained with acetone as trap. These results only suggest that the silene is not formed in the gas-phase reactions, but do require that if silenes *are* produced, rearrangement to a ketene is faster than trapping with benzaldehyde.





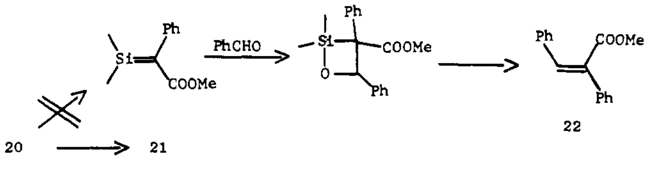
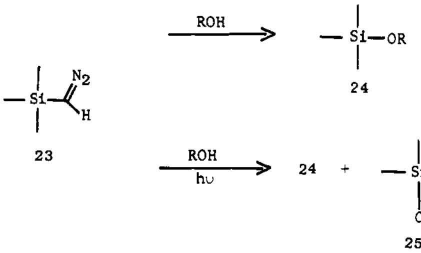


Table II. Photolysis of Trimethylsilyldiazomethane in Alcohols

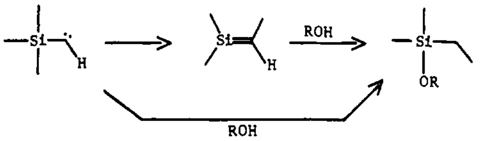
alcohol	yield, % **24**	**25**
MeOH	80	16
EtOH	45	51
i-PrOH	23	43
t-BuOH	0	45

Thus the weight of the evidence is against silene formation in the gas phase. Although it is tempting to generalize, the results in solution leave the question open. At present a reaction proceeding through a silene cannot be differentiated from the direct attack on silicon by alcohol postulated earlier. In another case, however, the weight of the evidence lies on the side of silene formation.

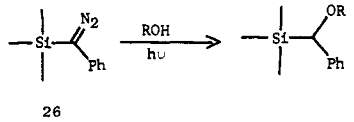
Trimethylsilylcarbene itself is known to produce trimethylsilene under a variety of conditions.[17] Although thermal decomposition in alcohols of trimethylsilyldiazomethane (**23**), with or without Lewis acid catalysis, led only to a cleavage product **24**, photolysis gave **25** as well (Table II).



Cleavage must occur through attack by the alcohol on silicon. Accordingly, the absence of such cleavage in the reaction with *tert*-butyl alcohol suggests that a mechanism for formation of **25** by attack on silicon is unlikely. In this case, the intervention of a silene seems probable.



Phenyltrimethylsilyldiazomethane (**26**) gave only the product of insertion into the O–H bond of the alcohol. Thus **2** finds itself intermediate between trimethylsilylcarbene and phenyltrimethylsilylcarbene in its ability to give the rearranged product attributable to a silene. Perhaps the fraction of rearrangement can be used to order the stability of the carbenes, with the least stable being most susceptible to rearrangement.



Summary

The formation of compounds of type **9** on pyrolysis of trimethylsilyl diazoacetates in the gas phase followed by treatment with alcohols does not involve simple silene formation followed by alcoholysis. The immediate precursor to **9** is ketene **19**. If **19** is itself formed from a silene, the reaction must be much faster than conventional silene trapping reactions. The weight of evidence is against silene formation in the gas phase. In solution, however, we regard silene formation as much more

Table III. Analytical Results and NMR Spectra of the Products

	compd	anal./mass spectrum found (calcd), %		NMR, δ ppm[a] (CCl_4)
		C	H	
6	$Me_3SiCH(OMe)CO_2Me$	47.60 (47.69)	9.13 (9.15)	0.08 (s) 9 H, 3.32 (s) 3 H, 3.57 (s) 1 H, 3.66 (s) 3 H
7	$Me_3SiCH(OMe)CO_2Et$	50.25 (50.49)	9.49 (9.53)	0.00 (s) 9 H, 1.18 (t) 3 H, 3.25 (s) 3 H, 3.45 (s) 1 H, 4.08 (q) 2 H
7-d_4	$Me_3SiCD(OCD_3)CO_2Et^b$			0.09 (s) 9 H, 1.25 (t) 3 H, 4.19 (q) 2 H
8	$Me_3SiCH(OEt)CO_2Me$	50.40 (50.49)	9.57 (9.53)	0.08 (s) 9 H, 1.18 (t) 3 H, 3.68 (s) and 3.0-3.8 (m) 6 H
8-d_4	$Me_3SiCD(OEt)CO_2CD_3^b$			0.05 (s) 9 H, 1.06 (t) 3 H, 3.21 (m) 1 H, 3.68 (m) 1 H
9	$Me_2Si(OMe)CHMeCO_2Et$	50.81 (50.49)	9.67 (9.53)	0.12 (s) 6 H, 1.17 (d) and 1.22 (t) 6 H, 2.08 (q) 1 H, 3.41 (s) 3 H, 4.09 (q) 2 H
9-d_4	$Me_2Si(OCD_3)CDMeCO_2Et^b$			0.16 (s) 6 H, 1.18 (s) 3 H, 1.22 (t) 3 H, 4.11 (q) 2 H
15	$Me_2Si(OMe)CH_2CHDCOOEt$	191.1023 (191.1083)		0.13 (s) 6 H, 1.17 (br s) 3 H, 1.23 (t) 3 H, 3.42 (s) 3 H, 4.05 (q) 2 H
	$Me_3SiCH(OEt)CO_2Et$	52.93 (52.90)	9.90 (9.86)	0.00 (s) 9 H, 1.10 (t) and 1.19 (t) 6 H, 2.9-3.8 (m) and 3.58 (s) 3 H, 4.08 (q) 2 H
17a	$Me_2Si(OEt)CHMeCO_2Et$	52.86 (52.90)	9.83 (9.87)	0.12 (s) 6 H, 1.0-1.4 (m) 9 H, 2.05 (q) 1 H, 3.66 (q) 2 H, 4.06 (q) 2 H
17b	$Me_2Si(OMe)CHMeCO_2Me^c$			0.5 (d) 6 H, 1.12 (d) 3 H, 1.8-2.2 (m) 1 H, 3.28 (s) 3 H, 3.47 (s) 3 H
	$Me_3SiCH(O\text{-}i\text{-}Pr)CO_2Et^{d,e}$	55.20 (55.00)	10.28 (10.15)	0.05 (s) 9 H, 1.06 (d), 1.17 (d), and 1.25 (t) 9 H, 3.3-3.8 (m) and 3.77 (s) 2 H, 4.11 (q) 2 H
	$Me_3SiCH(OEt)CO_2\text{-}i\text{-}Pr^d$			0.00 (s) 9 H, 0.9-1.3 (m) 9 H, 3.53 (s) 1 H, 4.05 (q) 2 H, 4.6-5.2 (m) 1 H
	$Me_3SiCH(O\text{-}i\text{-}Pr)CO_2\text{-}i\text{-}Pr$	56.78 (56.85)	10.47 (10.41)	0.02 (s) 9 H, 0.9-1.3 (m) 12 H, 3.2-3.8 (m) and 3.68 (s) 2 H, 4.7-5.2 (m) 1 H
	$Me_2Si(O\text{-}i\text{-}Pr)CHMeCO_2Et$	55.37 (55.00)	10.25 (10.15)	0.03 (s) 3 H, 0.08 (s) 3 H, 1.0-1.3 (m) 12 H, 2.00 (q) 1 H, 3.5-3.8 (m) 1 H, 4.02 (q) 2 H
	$Me_3SiCH(O\text{-}t\text{-}Bu)CO_2Et$	56.56 (56.85)	10.22 (10.41)	0.01 (s) 9 H, 1.08 (s) and 1.20 (t) 12 H, 3.72 (s) 1 H, 4.02 (q) 2 H
	$Me_3SiCH(O\text{-}t\text{-}Bu)CO_2\text{-}t\text{-}Bu^f$			0.05 (s) 9 H, 1.10 (s) 9 H, 1.42 (s) 9 H, 3.67 (s) 1 H
	$Me_3SiCH(OEt)CO_2\text{-}t\text{-}Bu$	56.95 (56.85)	10.50 (10.41)	0.08 (s) 9 H, 1.14 (t) 3 H, 1.43 (s) 9 H, 3.1-3.9 (m) and 3.48 (s) 3 H
	$Me_2Si(O\text{-}t\text{-}Bu)CHMeCO_2Et$	56.59 (56.85)	10.21 (10.41)	0.13 (s) 6 H, 1.21 (s) and 1.0-1.4 (m) 15 H, 1.97 (q) 1 H, 4.02 (q) 2 H
	$Me_3SiCD(OMe)CO_2Et$			0.00 (s) 9 H, 1.20 (t) 3 H, 3.27 (s) 3 H, 4.08 (q) 2 H
	$Me_3SiCD(OMe)CO_2Me$			0.03 (s) 9 H, 3.30 (s) 3 H, 3.63 (s) 3 H
	$Me_3SiCD(OEt)CO_2Me$			0.03 (s) 9 H, 1.13 (t) 3 H, 3.0-3.8 (m) and 3.61 (s) 5 H
	β-lactone **18**[f]			0.17 (s) 9 H, 3.1-3.5 (m) 1 H, 3.7-4.1 (m) 1 H, 4.1-4.4 (m) 1 H
	ketene **19a**[f]			0.22 (s) 6 H, 1.20 (t) 3 H, 1.62 (s) 3 H, 3.68 (q) 2 H
	ketene **19b**[f]			0.22 (s) 6 H, 1.61 (s) 3 H, 3.43 (s) 3 H
	ketene **21**	63.85 (64.04)	6.83 (6.84)	0.33 (s) 6 H, 3.47 (s) 3 H, 6.8-7.5 (m) 5 H
27a	$Me_3SiCH(OMe)Ph$	68.05 (67.98)	9.38 (9.34)	−0.05 (s) 9 H, 3.24 (s) 3 H, 3.83 (s) 1 H, 6.9-7.4 (m) 5 H
27b	$Me_3SiCH(OEt)Ph$	69.32 (69.17)	9.65 (9.67)	−0.04 (s) 9 H, 1.16 (t) 3 H, 2.9-3.7 (m) 2 H, 3.93 (s) 1 H, 6.8-7.2 (m) 5 H
27c	$Me_3SiCH(O\text{-}i\text{-}Pr)Ph$	69.44 (69.58)	9.77 (9.88)	−0.05 (s) 9 H, 1.10 (d) 6 H, 3.2-3.7 (m) 1 H, 4.10 (s) 1 H, 6.9-7.3 (m) 5 H

[a] Proton chemical shift of $CHCl_3$ (δ 7.25) was used as an internal standard. [b] In $CDCl_3$. [c] In C_6D_6. [d] Data of the mixture are given since these compounds could not be separated from each other by gas chromatography. [e] Prepared independently by photolysis of ethyl trimethylsilyldiazoacetate in diisopropyl ether. [f] No data for analysis are given because of the small yield or instability.

probable, although mechanisms bypassing silenes are still not excluded.

Experimental Section

General. NMR spectra were obtained on Varian A-60D, A-60A, or XL-100 spectrometers. Infrared spectra were measured either on an Hitachi EVI-G3 or Perkin-Elmer 238B spectrometers. Mass spectra were obtained on Nippon Denshi JMF-07, Hitachi RMU-6M, AEI MS 1073, or AEI MS 9 spectrometers. Gas chromatography-mass spectrometry was conducted on an AEI MS 1073 spectrometer equipped with a Data General NOVA 2 computer. Mass spectra were recorded at 3 s/decade with ionization energy of 70 eV. Diazo compounds **1a, 1b,** and methyl dimethylphenyldiazoacetate were prepared by the method of Schöllkopf.[8] Diazo compound **23** was made by the method of Seyferth[18] and **26** by that of Brook.[19]

Photolysis of Ethyl Trimethylsilyldiazoacetate (1a) in Alcohols (Table I, Footnote *a*). A solution of 345 mg of **1** and 1274 mg of methanol was cooled with running water in a Pyrex tube and irradiated through Pyrex with a Rikosha 400-W high-pressure mercury lamp for 5 h. After evaporation of the methanol the residue was separated by gas chromatography on a 4 mm × 2 m stainless steel column packed with 15% SF-96 on Celite 545 at 100 °C. The products were characterized by NMR, IR, and elemental analyses as shown in Table III. Photolyses of **1a** in ethanol, 2-propanol, and *tert*-butyl alcohol were carried out in a similar manner. Spectroscopic data of the products are given in Table III.

Photolysis of Ethyl Trimethylsilyldiazoacetate (1a) in Methanol (Table I, Footnote *b*). Typically 10–12 mg of **1a** was dissolved in 0.1 mL of dry methanol and the solution placed in a quartz tube fitted with a rubber septum and drying tube. The quartz tube was then immersed in a water-cooled quartz jacket and the solution photolyzed in a Rayonet reactor with 16 2537-Å lamps. Progress of the photolysis was followed by UV spectroscopy. Complete photolysis took about 1.5 h. Photolysis in tetradeuteriomethanol was conducted under the same conditions. The products were separated by gas chromatography on a 6 ft × $^1/_8$ in. column packed with 3% Dexil 400 GC/Chromosorb WHP 80/100 using a Hewlett-Packard 5750 gas chromatograph. Spectroscopic data of the products are given in Table III.

Photolysis of Ethyl Trimethylsilyldiazoacetate (1a) in Methanol in the Presence of Lithium Chloride (Table I, Footnote *a*). A solution of 1 mmol of **1a**, 10 mL of methanol, and 1 mmol of lithium chloride was irradiated with a Rikosha high-pressure mercury lamp until the evolution of nitrogen ceased. Analysis by gas chromatography showed the presence of the four products given in Table I. Ethyl α-chlorotrimethylsilylacetate was not detected. This compound was prepared independently in 80% yield from the photolysis of **1a** in *tert*-butyl chloride.

Photolysis of Ethyl Trimethylsilyldiazoacetate (1a) in Methanol in the Presence of Lithium Bromide. A solution of 1 mmol of **1a**, 10 mL of methanol, and 1 mmol of lithium bromide was irradiated with a Rikosha high-pressure mercury lamp until the evolution of nitrogen ceased. Results are given in Table I. Ethyl α-bromotrimethylsilylacetate was not formed. This compound was prepared independently in 80% yield from the photolysis of **1a** in ethyl bromide.[20]

Photolysis of Ethyl Trimethylsilyldiazoacetate (1a) in Methanol-d_1. A solution of 2 mmol of **1a** and 2 mL of methanol-d_1 was irradiated with a Rikosha high-pressure mercury lamp. Separation of the products and determination of the relative yields were done by gas chromatography. Spectroscopic data appear in Table III.

Decomposition of Ethyl Trimethylsilyldiazoacetate (1a) by Hydrochloric Acid in Methanol. A solution of 1 mmol of **1a**, 1 mL of methanol, and 0.03 mmol of hydrochloric acid was allowed to stand in the dark at room temperature. Ethyl methoxyacetate was obtained by gas chromatography.

Thermal Decomposition of Ethyl Trimethylsilyldiazoacetate (1a) in Methanol. A solution of 170 mg of **1a** and 2 g of methanol was heated in a sealed tube at 110 °C for 2 h. Ethyl methoxyacetate (90%) and methyl methoxyacetate (10%) were obtained by gas chromatography.

Thermal Decomposition of Ethyl Trimethylsilyldiazoacetate (1a) in Ethanol. A solution of **1a** and excess ethanol was heated in a sealed tube at 140 °C for 2 h. Ethyl ethoxyacetate was obtained by gas chromatography.

Pyrolysis of Methyl Trimethylsilyldiazoacetate (1b) in the Gas Phase. The flash pyrolysis apparatus consisted of a Pyrex pyrolysis tube (1 × 37 cm) heated by an electric oven. The sample was introduced into the hot zone through a serum cap using a 100-μL syringe. The apparatus was maintained at 2 Torr and the products were collected in a trap cooled with dry ice/acetone or liquid nitrogen. In a typical procedure the apparatus was heated to 360 °C and 1.024 g of **1b** introduced through the rubber septum with a syringe. Separation of the reaction mixture on a 4 mm × 2 m gas chromatography column packed with 15% SF-96 on Celite 545 at 84 °C gave ketene **19** and lactone **18**. Spectroscopic data can be found in Table III.

Reaction of Ketene 19 with Alcohols. A solution of **19** and excess ethanol was warmed at 60 °C for 30 min. Analysis of the reaction mixture by gas chromatography showed the formation of ethyl α-dimethylethoxysilylpropionate.

Reaction of the Pyrolysate of Methyl Trimethylsilyldiazoacetate (1b) with Ethanol. Methyl trimethylsilyldiazoacetate (**1b**, 203 mg) was pyrolyzed in the gas phase at 360 °C at 2 Torr, and then 6 mL of ethanol was added to the pyrolysate. Esters **7** and **17** and lactone **18** were obtained by gas chromatography.

Pyrolysis of Ethyl Trimethylsilyldiazoacetate (1a) in the Gas Phase. **1a** (0.7651 g) was pyrolyzed in a similar manner at 360 °C at 2 Torr. Separation of the reaction mixture by gas chromatography gave ketene **19a** in 11% yield.

Reaction of the Pyrolysate of Methyl Trimethylsilyldiazoacetate (1b) with Methanol. **1b** (0.150 mL) was evaporated through an empty quartz tube at 0.6 Torr and 360 °C. The pyrolysate was collected on a cold finger maintained at liquid nitrogen temperature. Methanol (0.800 mL) was added at the end of the pyrolysis in three portions to wash the pyrolysate off the cold finger. The solution was allowed to sit at liquid nitrogen temperature for 10 min and then warmed to −78 °C before it was allowed to come to room temperature. Gas chromatographic analysis revealed **6** and **17b**.

Reaction of the Pyrolysate of 1b with Tetradeuteriomethanol. Diazo compound **1b** was evaporated through an empty Pyrex tube and condensed as above at −196 °C. The pyrolysate was washed off the cold finger with tetradeuteriomethanol and the rearranged product **17** examined by NMR spectroscopy. The total absence of methoxy signals revealed that both alkoxy groups had exchanged.

Copyrolysis of Methyl Trimethylsilyldiazoacetate (1b) with Ethanol. Copyrolysis was carried out with a 28 × 1 cm Pyrex vertical tube packed with Pyrex chips and heated by an electric oven. A flow of nitrogen (30 mL/min) was maintained. A solution of 0.2032 g of **1b** and 2 mL of ethanol was dripped through the rubber serum cap with a 1-mL syringe into the Pyrex tube heated at 380 °C. Separation of the reaction mixture by gas chromatography gave **7** (33%) and **17** (4%).

Pyrolysis of Methyl Dimethylphenylsilyldiazoacetate in the Gas Phase. Diazo compound (271 mg) was pyrolyzed through the Pyrex tube heated at 400 °C at 2 Torr. Methoxydimethylsilylphenylketene (**21**) was obtained by gas chromatography in 51% yield.

Copyrolysis of Methyl Dimethylphenylsilyldiazoacetates with Benzaldehyde or Acetone. A solution of diazo compound and excess carbonyl compound was copyrolyzed using the vertical tube with a nitrogen flow at 400 °C. Separation of the reaction by gas chromatography gave ketene **21**. No **22** could be detected.

Thermal Decomposition of Trimethylsilyldiazomethane (23) in Ethanol. A solution of **23** and excess ethanol was allowed to stand at room temperature for 4 days. Ethoxytrimethylsilane (**24**) was formed, but no ethoxyethyldimethylsilane could be found. Compound **24** was also produced by refluxing a solution of **23** in excess ethanol.

Decomposition of Trimethylsilyldiazomethane (23) by Boron Trifluoride Etherate or Copper(I) Chloride in Ethanol. Boron trifluoride etherate (1 μL) was added to a solution of **23** and excess ethanol cooled with an ice bath. Ethoxytrimethylsilane was obtained by gas chromatography. A catalytic amount of copper(I) chloride was added to a solution of **23** and excess ethanol. Ethoxytrimethylsilane was obtained by gas chromatography.

Photolyses of Trimethylsilyldiazomethane (23) in Alcohols. A solution of ca. 0.3 mmol of **23** and excess alcohol was irradiated with a Rikosha high-pressure mercury lamp. Separation of the reaction mixture by a 4 mm × 1.8 m column packed with 10% KF-96 on Celite 545 at 37 °C gave alkoxytrimethylsilane (**24**) and alkoxyethyldimethylsilane (**25**). The yields are listed in Table II. The products were identified by comparison with the spectra of authentic samples, prepared from the reactions of trimethylchlorosilane and dimethylethylchlorosilane with alcohols in the presence of pyridine.

Photolysis of Trimethylsilylphenyldiazomethane (26) in Methanol. A solution of 114 mg of **26** and 1.5 mL of methanol was irradiated with a Rikosha high-pressure mercury lamp for 3 h. Separation of the reaction mixture by gas chromatography gave an OH insertion product (**27a**) in 61% yield.

Photolysis of Trimethylsilylphenyldiazomethane (26) in Ethanol. A solution of 90 mg of **23** and 1.5 mL of ethanol was irradiated with a Rikosha high-pressure mercury lamp. Separation of the reaction mixture by gas chromatography gave an OH insertion product (**27b**) in 48% yield.

Photolysis of Trimethylsilylphenyldiazomethane (26) in 2-Propanol. A solution of 103 mg of **23** and 1.5 mL of 2-propanol was irradiated with a Rikosha high-pressure lamp. Separation of the reaction mixture by gas chromatography gave an OH insertion product (**27c**) in 27% yield.

References and Notes

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A Method for Effecting the Equivalent of a de Mayo Reaction with Formyl Acetic Ester[1a]

Bruce A. Pearlman[1b]

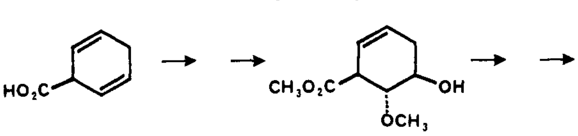
Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. *Received February 24, 1978*

Abstract: Both Woodward reserpine precursor **1** and Corey prostaglandin precursor **3** are monocyclic compounds with vicinal carboxaldehyde and acetic ester appendages. Disconnection of these appendages (along with disconnection of the two oxygen substituents of **1**) generates hypothetical precursors (1,4-dihydrobenzoic acid and *cis*-cyclopentene-3,5-diol) both of which are readily available. Therefore, both reserpine and the prostaglandins might become available by short synthetic sequences if a method existed for the placement of vicinal carboxaldehyde and acetic ester appendages onto double bonds. This paper reports a five-step sequence that accomplishes this transformation for the case of 4-hydroxycyclohexene.

Introduction

Reserpine (**2**) and the prostaglandins (for example, PGF$_{2\alpha}$ [**4**]) are natural products whose physiological effects make them of great value in medicine, reserpine as an antihypertensive[2] and the prostaglandins as agents for the regulation of fertility.[3] Since their structures are relatively complex, total synthesis would seem to be an unlikely means of procurement but, due to the elegant and classic work of Woodward[4] and Corey,[5] some pharmaceutical companies have seriously considered the use of total synthesis to obtain their supplies.[2,5c,6] Not only are these two syntheses commercially feasible, but they also were considered by I. Fleming to be so artistically "beautiful" [7] that he arranged his book "Selected Organic Syntheses" so as to present them as the final two chapters.

However, these two syntheses have one striking feature in common: namely, that cyclic compounds with vicinal carboxaldehyde and acetic ester appendages (**1** and **3**) are key intermediates. Moreover, disconnection of these appendages (along with disconnection of the two oxygen substituents of **1**) generates olefins that are readily available (1,4-dihydrobenzoic acid[8] and *cis*-cyclopentene-3,5-diol,[9] respectively). *Thus, both reserpine and the prostaglandins might become available by even simpler synthetic routes if a sufficiently simple method existed for the placement of vicinal carboxaldehyde and acetic ester appendages onto double bonds.*



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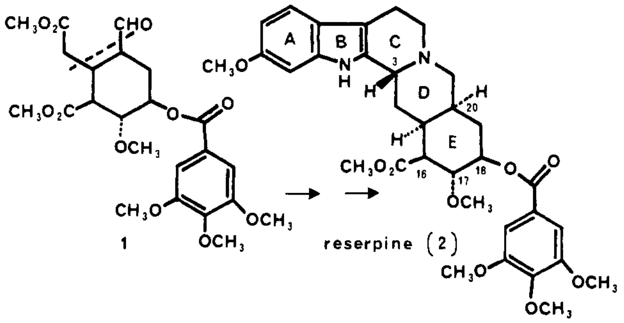
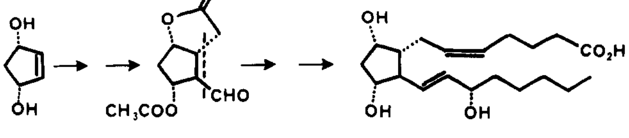


1 reserpine (**2**)



3 PGF$_{2\alpha}$ (**4**)

Actually, sequences which effect attachment of vicinal two-carbon and one-carbon appendages onto a ring are known.[10-15] However, none of this methodology was deemed appropriate for the two intended applications. Therefore, research directed toward filling this gap in synthetic methodology was undertaken.

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