were identified and found in the ratio 30.9:69.1. The structure of **3a** was further confirmed by transformation to (4-phenylbutyl)dimethylchlorosilane [bp 148° (19 mm), $n^{20}\mathrm{D}$ 1.4999, $d^{20}{}_4$ 0.9951]. To our knowledge this is the first clear evidence that shows free-radical migration of the phenyl group from carbon to silicon. The ratio of the products depends on the molar ratio of the starting hydrosilane to DTBP and the results are shown in Table I. Similar results with (4-*p*-tolylbutyl)dimethylsilane [**1b**, bp 132° (17 mm), $n^{20}\mathrm{D}$ 1.4917, $d^{20}{}_4$ 0.8684] and (4-phenylpentyl)dimethylsilane [**1c**, bp 108° (5 mm), $n^{20}\mathrm{D}$ 1.4940, $d^{20}{}_4$ 0.9779] are also listed in Table I.

Table I. Reaction of (4-Arylbutyl)dimethylsilanes with DTBP at 135.0°

Substrate	DTBP/ substrate (molar ratio)	Rearrangement product, %	Cyclization product, %
$C_6H_5(CH_2)_4SiMe_2H$	0.343	30.9	69.1
(**1a**)	0.767	25.5	74.5
	1.372	21.2	78.8
p-$CH_3C_6H_4(CH_2)_4SiMe_2H$	0.423	37.8	62.2
(**1b**)	0.708	33.6	66.4
	1.113	28.0	72.0
	2.012	23.7	76.3
$C_6H_5CH(CH_3)(CH_2)_3SiMe_2H$	0.697	72.0	28.0
(**1c**)	0.760	69.2	30.8

We have examined further a number of other compounds of a general formula of $PhCHY(CH_2)_nSiMe_2H$ for a possible competition of rearrangement *vs.* cyclization. Table II lists the results. For compounds of $n = 0, 1, 4$, and 5, neither cyclization nor rearrangement was observed. Only cyclization occurred for compounds of $n = 2$ as reported previously.[4] It is interesting to note that homolytic aromatic substitution, affording a five-membered ring compound which is not sterically much strained, is completely suppressed.

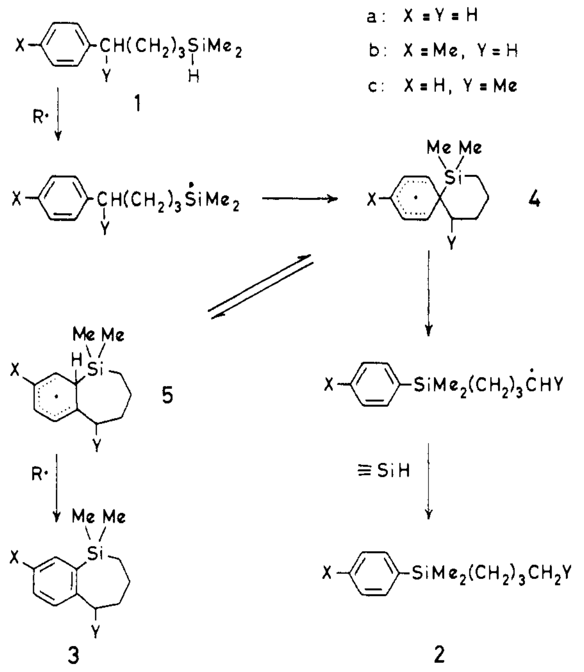
Table II. Reaction of $C_6H_5CHY(CH_2)_nSiMe_2H$ with DTBP at 135.0°

Substrate	*n*	Y	Rearrangement	Cyclization
7a	0	H	No	No
7b	0	Me	No	No
7c	0	Ph	No	No
8	1	H	No	No
6a	2	H	No	Yes
6b	2	Me	No	Yes
6c	2	Ph	No	Yes
1a	3	H	Yes	Yes
1c	3	Me	Yes	Yes
9	4	H	No	No
10	5	H	No	No

These results now suggest the following mechanism (Chart I) for the competition of rearrangement *vs.* cyclization of **1** involving a spirocyclohexadienyl radical (**4**) as an intermediate.

For compounds **1**, there may exist a subtle equilibrium between **4** and **5**. It is notable in this connection that increasing the amount of DTBP in reaction mixtures resulted in an increased amount of cyclization products and that introduction of a methyl group into the benzylic position favored the rearrangement. However, for compounds of $n = 2$ (**6**), the corresponding intermediate spiro radicals may collapse rapidly to cyclic intermediates corresponding to **5** leading to cyclization, since the ring size favors the latter radicals. The fact that neither rearrangement nor cyclization took place at all with $ArCHY(CH_2)_nSiMe_2H$, where $n = 0, 1, 4$, and 5, is also compatible with the intermediacy of the spiro radicals, since the formation of spiro intermediates of three-, four-, seven-, and eight-membered rings must be sterically strained.

Chart I



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Photochemically Induced Rearrangement of Ketene *via* an Oxirene Intermediate

Sir:

The photolysis of ketene has been studied for many years, sometimes because of its own inherent interest and more often in a peripheral manner to its use as a source of methylene radicals.[1] Detailed experiments have shown the presence of long-lived excited states through quantum yields for photodecomposition less than unity and variable with wavelength, pressure, and temperature for absorbed wavelengths ≥ 3130 Å.[2]

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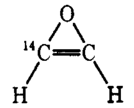
[1] (a) W. B. Demore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964); (b) J. A. Bell, *Progr. Phys. Org. Chem.*, **2**, 1 (1964); (c) H. M. Frey, *Progr. Reaction Kinet.*, **2**, 131 (1964); (d) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

[2] A. N. Strachan and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **76**, 3258 (1954); G. A. Taylor and G. B. Porter, *J. Chem. Phys.*, **36**, 1353

Since no light emission has been observed under these conditions,[3] the quantum yield deficit has been attributed to radiationless deactivation processes of an essentially unknown character. Our current experiments on the photolysis of $^{14}CH_2CO$ show a pressure-dependent yield of ^{14}CO, indicating the involvement of the oxirene intermediate **I**, which after rearrangement is then capable both of decomposition (either to $^{14}CH_2$ + CO or CH_2 + ^{14}CO) and of deexcitation without decomposition. The oxirene structure has long been postulated as an intermediate in various reactions,[1d,4] and definitely identified as being present in gas-phase photolyses of α-diazoketones[5] and alkyl diazoacetates.[6]



I

The yields of ^{14}CO from $^{14}CH_2CO$ photolysis are shown in Table I for a variety of experimental conditions. The experimental procedures in the photolysis of tracer-labeled ketene[7-9] and in measurement of the products by radio gas chromatography[10] are both standard methods which have been described previously. We have not yet carried out the difficult isolation of unreacted ketene for determination of progressive scrambling in it.

The basic observation of an appreciable yield of ^{14}CO from the photolysis of $^{14}CH_2CO$ suggests either (a) active participation of the oxirene intermediate I; (b) the reaction of $^{14}CH_2$ with trace impurities of O_2;[8,9] or (c) $CH_2{}^{14}CO$ as an isotopic labeling impurity in $^{14}CH_2CO$. The isotopic integrity of the original $^{14}CH_2CO$ (made by pyrolysis of acetic anhydride from New England Nuclear Corporation) was established as 99.5% by two other reactions—pyrolysis in the presence of HBr and Hg photosensitization.[11] The 0.5% ^{14}CO found from $^{14}CH_2CO$ by each of these experiments could indicate either an isotopic impurity of ≤0.5% $CH_2{}^{14}CO$, or an oxirene intermediate in these processes as well. While further tests will be necessary to establish the source of this residual ^{14}CO, a slight variability in ^{14}CO yield from batch to batch of $^{14}CH_2CO$ indicates that at least part of the 0.5% is an impurity in isotopic position.

Table I. Observed Yields of ^{14}CO formed during Photolysis of Oxygen-Free $^{14}CH_2CO$

λ 3130 Å							λ 3340 Å						
Composition, Torr		Photolysis time, min	% ketene decomposed	% yields		%[c] photolytic scrambling	Composition, Torr		Photolysis time, min	% ketene decomposed	% yields		%[c] photolytic scrambling
$^{14}CH_2CO$	C_2H_4			^{14}CO[a]	$^{14}CO_2$[b]		$^{14}CH_2CO$	Other			^{14}CO[a]	$^{14}CO_2$[b]	
3.7	3,030	120	2	1.4	0.00	0.9	3.6	387 C_5D_{12}	180	4	1.6	0.14	1.1
3.7	757	120	3	2.8		2.3	7.4	391 C_5H_{12}	360	4	1.7		1.2
0.45	762	120	1	3.0		2.5	7.6	397 C_5H_{12}	720	14	1.9		1.4
3.0	404	60	4	3.7		3.2	7.6	397 C_5H_{12}	1080	18	2.0		1.5
3.7	197	120		3.7		3.2	29.0	301 C_2H_4	180	8	2.3		1.8
3.7	95	120	6	4.5		4.0	3.6	3.6 C_2H_4	190	15	6.2	0.05	8.0
3.6	3.6	30	4	3.8	0.07	4.5	3.6		180	18	6.2	0.09	10.2
0.06	0.6	120	25	6.0		6.0	3.6		60	6	5.3	0.14	8.4
3.6	0	30	5	3.8		5.6	3.6		20	2	4.9	0.26	7.2

[a] Per cent of total observed volatile activity; remainder is present in previously characterized products of $^{14}CH_2$ reactions. [b] When not listed, the $^{14}CO_2$ activity was not separated from the $^{14}CH_3$-CH_2CH_3 also formed in these unscavenged samples. [c] Per cent ^{14}CO formed in photolytic decomposition of ketene, after correction for assumed 0.5% $CH_2{}^{14}CO$ in $^{14}CH_2CO$.

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(11) The pyrolysis with HBr produced 0.50% ^{14}CO and 99.5% $^{14}CH_3Br$. Hg photosensitization gave 0.43% ^{14}CO and 99.6% known $^{14}CH_2$ products. The original $^{14}CH_2CO$ contained approximately 6% ^{14}C atoms in the methylenic position; inactive ketene was added in many experiments.

The reaction of $^{14}CH_2$ with O_2, while very efficient, forms ^{14}CO and $^{14}CO_2$ in equal amounts,[8,9,12] and adventitious O_2 can thus be monitored through the detection of $^{14}CO_2$. For many of the samples in Table I, the $^{14}CO_2$ yield was measured and shown to be very much less than that of ^{14}CO, indicating that reaction with trace O_2 was at most a minor source of ^{14}CO in these experiments.

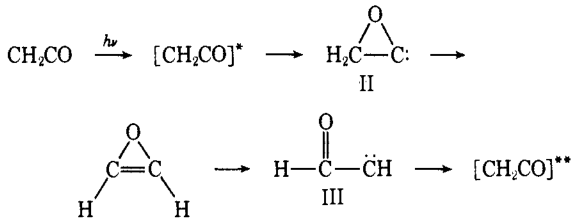
A possible oxirene intermediate of another type—formed by CH_2 attack on CH_2CO—can be eliminated as the major source of ^{14}C scrambling by the observation of appreciable ^{14}CO in experiments with low percentages of ketene, *e.g.*, 2% *vs.* 98% ethylene. In these low-ketene experiments, secondary attack on $^{14}CH_2CO$ by photolytically produced radicals is essentially negligible. In pure ketene photolyses, however, approximately two molecules of ketene are removed for every molecule decomposed photolytically. Assuming that no ^{14}C scrambling occurs in these radical attacks, we have calculated in Table I a per cent scrambling of ^{14}C based on photolytically decomposed molecules alone.

The quantum yield for ketene photodecomposition varies from about 0.1 at 3000 Torr to unity at the lowest pressures.[2] The quantum yield for dissociation with scrambling of ^{14}C is thus about 70 times larger at low pressure than at high pressure. Although it cannot be conclusively proven, the scrambling of ^{14}C position does not appear to come from a photoexcited state with a lifetime appreciably different from that exhibited by the bulk of the photoexcited ketene molecules.

The time dependence of the ^{14}CO yields in two sets of comparable experiments at 3340 Å indicates that most of the reactions are single-photon processes, but the slow percentage increase of ^{14}CO with time indicates that some $^{14}CH_2CO$ molecules have rearranged without decomposition with the first photon, and are then subsequently decomposed by a second photon. We assume that this rearranged product is ketene itself, although nothing in our experiments rules out the possibility of its being some other rearranged C_2H_2O molecule—for example, stabilized oxirene itself. Since oxirene is unknown, its properties cannot be distinguished from those of ketene, and in our experiments, the properties of oxirene, if it exists as a stable molecule, would be expected to be essentially identical with those of ketene.

The scrambling of ^{14}C prior to decomposition is excellent evidence for the existence of the symmetrical intermediate with equivalent carbon positions, as in I. The mechanism of formation of this intermediate is of course speculative, but could involve other intermediates such as the carbenes II and III. A set of plausible steps for this reaction includes each of these intermediates in succession, as shown in sequence 1. No evidence exists in our experiments for the presence of either II or III, and the observations could equally well be described by a concerted mechanism including the oxirene structure I at some stage in the reaction.

Since the $Hg(^3P_1)$ photosensitization of ketene produces only 0.5% ^{14}C scrambling, we postulate that an excited triplet state is not the precursor of the oxirene intermediate. The initial excited ketene $(CH_2CO)^*$ is probably an electronically excited singlet state, capable of the rearrangement to the cyclic carbene II, while the final excited ketene $(CH_2CO)^{**}$ is probably the vibrationally excited ground state capable either of decomposition or stabilization. The stabilization path would then correspond to the radiationless pathway to ketene deexcitation.



(1)

The reactions shown in sequence 1 are not the only reaction paths available to excited ketene, for the per cent scrambling represents only a minor fraction of the total excited ketene species. The previous photolytic observations of oxirene intermediates have also shown that complete scrambling is not attained in those cases for which one of the substituents of the oxirene is an H atom.[5,6] These experiments involved two successive photolyses, the first causing a Wolff rearrangement and the second cleaving the substituted ketene formed in the first. Since oxirenes can now be expected in the second step, the question of oxirene participation in the Wolff rearrangement itself should be reexamined.

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[12] R. L. Russell and F. S. Rowland, unpublished experiments.

Structures of Stachysterone A, the First Natural 27-Carbon Steroid with a Rearranged Methyl Group, and Stachysterone B

Sir:

The bark of *Stachyurus praecox* SIEB. et ZUCC. ("kibushi" in Japanese) contains, in addition to β-ecdysone (**1**) (0.06% yield), four new phytoecdysones in yields of 0.002–0.004% each, which were designated stachysterones A (**2**), B (**3**), C (**4**), and D (**5**). All four have the molecular formula $C_{27}H_{42}O_6$ corresponding to loss of water from β-ecdysone. Structures of stachysterones C and D have been reported recently.[1] The moulting activities of stachysterones A, B, and C are comparable to those of other ecdysones but stachysterone D is only weakly active. The following data enable one to assign structure **2** to stachysterone A and **3** to stachysterone B. Although more than 30 ecdysones have been characterized during the past 3 years,[2] stachysterone A is most unique in that: (i) it is the first naturally occurring C_{27} steroid with a rearranged methyl group; (ii) retention of its biological activity casts intriguing problems pertaining to structure–activity correlations; (iii) the cooccurrence of

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