Silicon-directed Norrish Type I Cleavage of β-Trimethylsilyl Cycloalkanones

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The Me_3Si group in β-trimethylsilyl cycloalkanones was able to direct the Norrish type I cleavage by providing regioselectivity in the C-1–C-2 bond cleavage and by increasing the quantum yield and the reaction rate.

The Me_3Si group can stabilize a carboradical at the β-position by 2.6—2.8 kcal mol^{-1} (1 cal = 4.184 J).[1,2] Under mild conditions, β-trimethylsilyl carboradicals do not undergo the C–$SiMe_3$ bond cleavage to give $Me_3Si^{\cdot}$ and alkenes.[3—5] These properties may allow the Me_3Si group to direct certain reactions with radical intermediates. The products of these reactions still possess the Me_3Si group, which can be further utilized. Based on this concept, we studied the silicon-directed Norrish type I cleavage,[6,7] an unprecedented reaction. We report herein that photolysis of β-trimethylsilyl cycloalkanones gave vinylic or allylic silanes as the major products. The silicon-directed Norrish type I cleavage generally proceeded in a highly regioselective manner, with an improved quantum yield, and with a rate enhancement.

We irradiated β-(trimethylsilyl)cyclohexanone[8] (**1**) in anhydrous methanol containing $NaHCO_3$ (1.3 equiv.) using a 450 W medium pressure mercury lamp. Both of the products, alkenyl aldehyde (**2**) (45%) and ester (**3**) (43%), were generated through the C-1–C-2 bond cleavage (Scheme 1, Table 1).† Likewise, β-(trimethylsilyl)cyclopentanone (**4**) underwent photolysis to give products (**5**) (50%) and (**6**) (26%). These reactions, with excellent regioselectivity of the C-1–C-2 bond cleavage, are in sharp contrast with the 'normal' Norrish type I cleavage:[7] the ratio is 2:1 for the C-1–C-6 to C-1–C-2 bond cleavage in 3-methylcyclohexan-1-one[9] and for the C-1–C-5 to C-1–C-2 in 3-methylcyclopentan-1-one.[10] We believe that the highly regioselective C-1–C-2 bond cleavage in the photolysis of (**1**) and (**4**) comes from the stabilizing ability of the Me_3Si group towards β-carboradicals [*i.e.* (**20**)].

The silicon-directed photolysis was applicable to α-alkylated β-(trimethylsilyl)cycloalkanones. Thus, upon irradiation, (**7**)[8] gave products (**8**) (31%) and (**10**) (47%) mainly through C-1–C-2 cleavage (total yield 78%). Product (**9**), resulting from the C-1–C-6 cleavage, was isolated in only 4% yield. We also found that a β-Me_3Si group situated on a side chain

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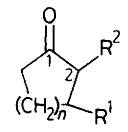
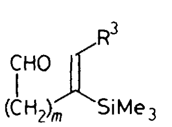
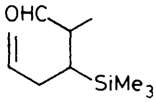
† All new compounds were fully characterized by NMR and IR spectroscopy, and mass spectrometry.



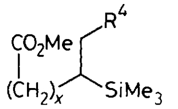
(1) $R^1 = SiMe_3$, $R^2 = H$, $n = 2$
(4) $R^1 = SiMe_3$, $R^2 = H$, $n = 1$
(7) $R^1 = SiMe_3$, $R^2 = Me$, $n = 2$
(11) $R^1 = H$, $R^2 = CH_2SiMe_3$, $n = 2$
(14) $R^1 = H$, $R^2 = CH_2SiMe_3$, $n = 1$



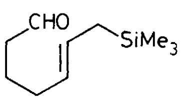
(2) $m = 3$, $R^3 = H$
(5) $m = 2$, $R^3 = H$
(8) $m = 3$, $R^3 = Me$



(9)



(3) $x = 3$, $R^4 = H$
(6) $x = 2$, $R^4 = H$
(10) $x = 3$, $R^4 = Me$



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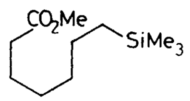

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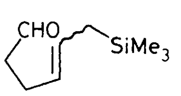

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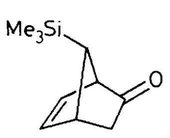

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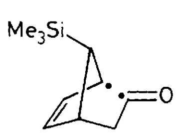

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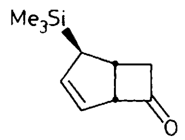

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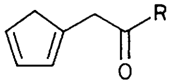

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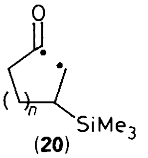

(20)

$n = 1, 2$

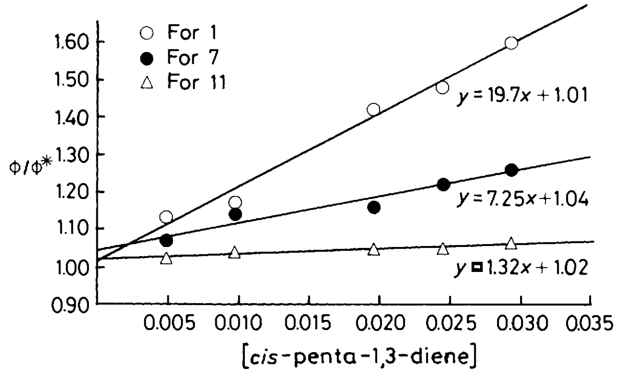

Figure 1. Stern–Volmer plots for Me_3Si substituted cyclohexanones; 3-(trimethylsilyl)cyclohexanone (**1**), 2-methyl-3-(trimethylsilyl)cyclohexanone (**7**), and 2-[(trimethylsilyl)methyl]cyclohexanone (**11**). The symbol ϕ represents the quantum yield of the reaction measured in the absence of *cis*-penta-1,3-diene and ϕ^* the quantum yield of reaction measured in the presence of *cis*-penta-1,3-diene.

Table 1. Norrish type I cleavage of β-trimethylsilyl cycloalkanones.

		Products (yield/%)	
Cycloalkanone	Conditions[a]	Alkenyl aldehyde	Ester
(**1**)	A	(**2**)(45)	(**3**)(43)
(**4**)	A	(**5**)(50)	(**6**)(26)
(**7**)	A	(**8**)(31) and (**9**)(4)	(**10**)(47)
(**11**)	A	(**12**)(68)	(**13**)(20)
(**14**)	A	(**15**)(87)	—
(**16**)[b]	B	(**18**)(51)	—

[a] *Reagents and conditions*: A, *hv*, (λ > 3000 Å), $NaHCO_3$, MeOH; B, *hv*, (λ > 3000 Å), ether. [b] Reaction occurred *via* (**17**) and did not produce (**19**).

(instead of on the ring) also provided a profound directing effect. In the photolyis of (**11**),[11] only allylic silane (**12**) (68%) and alkyl silane (**13**) (20%) were obtained. Similarly, (**14**)[11] yielded allylic silane (**15**) (87%) exclusively. The products (**12**), (**13**), and (**15**) were generated by cleavage of the C-1–C-2 bond in the starting cycloalkanones.

In these silicon-directed Norrish type I cleavages shown in Table 1, the Me_3Si moiety was not eliminated from diradical intermediates. This observation is in agreement with previous results obtained by others[3—5] and us:[12] $Me_3Si^{\cdot}$ is not eliminated from β-trimethylsilyl carboradicals.

Irradiation of bicyclic ketone (**16**)‡ in ether provided further evidence for the stability of β-trimethylsilyl radicals towards elimination. In (**16**), the Me_3Si moiety was perfectly aligned for elimination to form a conjugated diene (**19**), *via* a diradical intermediate (**17**). Nevertheless, bicyclic ketone (**18**) was formed in 51% yield and no cyclopentadienes were generated.

By using the procedure developed by Wagner and Spoerke,[13] we obtained quantum yields and rate constants for the photolysis of β-trimethylsilyl cyclohexanones (**1**), (**7**), and (**11**) (Table 2). The quantum yield of photolysis of (**1**) (ϕ = 0.501) was 2.5 times greater than that of cyclohexanone (ϕ = 0.20)[15] and 6.0 times greater than that of 3-methylcyclohexanone (ϕ = 0.083).[13] The rate constant of photolysis of (**1**) (2.53×10^8 s^{-1}) was 7.7 times greater than that of cyclohexanone (0.33×10^8 s^{-1})[13] and 10.1 times greater than that of 3-methylcyclohexan-1-one (0.25×10^8 s^{-1}).[13] Likewise, quantum yields and rate constants of photolysis of β-trimethylsilyl ketones (**7**) and (**11**) were also greater than those of 2-methylcyclohexan-1-one (see Table 2). Introduction of a β-Me_3Si group in cyclohexanones not only directed the C-1–C-2 bond cleavage, but also enhanced the quantum yield and the reaction rate. These results will be used in the development of photodegradable polymers.[14]

In the Stern–Volmer plots shown in Figure 1, the ϕ/ϕ^* intercepts of straight lines, representing cyclohexanones (**1**), (**7**), and (**11**), were close to 1.00. Thus these silicon-directed cleavages, similar to the 'normal' Norrish type I cleavage, went through the triplet state of cyclohexanones.[15]

In summary, an unprecedented silicon-directed Norrish type I cleavage was developed. Placement of a Me_3Si group at the β-position in cycloalkanones provided a regioselective

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‡ For (**16**): ^1H NMR ($CDCl_3$, 80 MHz) δ 0.00 (s, 9H, $SiMe_3$), 1.62—1.73 (m, 1H, $HCSiMe_3$), 1.91—1.99 (m, 2H, $CH_2C{=}O$), 2.98—3.03 (m, 1H, CH), 3.19—3.23 (m, 1H, CH), 5.99—6.16 (m, 1H, =CH), 6.44 (dd, *J* 5.2, 2.9 Hz, 1H, =CH); IR (neat) 3030 (=CH), 1740 (C=O), 1255 (Si–Me), 840 cm^{-1}.

Table 2. Comparison of quantum yields and reaction rates of cyclohexanones.

Ketone	Quantum yield (ϕ)[a]	Quantum yield ratio	Reaction rate ($1/\tau \times 10^8 s^{-1}$)	Rate ratio
(**1**)	0.501	(**1**)/(**21**) = 2.5 (**1**)/(**22**) = 6.0	2.53	(**1**)/(**21**) = 7.7 (**1**)/(**22**) = 10.1
Cyclohexanone (**21**)[b]	0.20		0.33	
3-Methylcyclohexan-1-one (**22**)[b]	0.083		0.25	
(**7**)	0.545	(**7**)/(**23**) = 1.1	6.90	(**7**)/(**23**) = 1.5
2-Methylcyclohexanone (**23**)[b]	0.50		4.7	
(**11**)	0.592	(**11**)/(**23**) = 1.2	37.9	(**11**)/(**23**) = 8.1

[a] It was measured based on 12—20% disappearance of ketones. [b] See ref. 15.

control in cleavage of the C-1–C-2 bond in the Me_3SiC–C-2–C-1(=O)–C_ω moiety. The quantum yields and the photolysis rates were also increased. This new reaction should be useful in the synthesis of vinylic and allylic trimethylsilanes.

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