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

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The Me₃Si 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 Me₃Si 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–SiMe₃ bond cleavage to give Me₃Si and alkenes.^{3–5} These properties may allow the Me₃Si group to direct certain reactions with radical intermediates. The products of these reactions still possess the Me₃Si 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)cyclohexanone⁸ (1) in anhydrous methanol containing NaHCO₃ (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-methylcyclopentan-1-one⁹ 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 Me₃Si 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 -Me₃Si group situated on a side chain

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



Figure 1. Stern–Volmer plots for Me₃Si 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) | А | (2)(45) | (3)(43) | |
| (4) | Α | (5)(50) | (6)(26) | |
| (7) | Α | (8)(31) and (9)(4) | (10)(47) | |
| (11) | Α | (12)(68) | (13)(20) | |
| (14) | Α | (15)(87) | | |
| (16) ^b | В | (18)(51) | | |

^a Reagents and conditions: A, hv, ($\lambda > 3000$ Å), NaHCO₃, MeOH; B, hv, ($\lambda > 3000$ Å), ether. ^b Reaction occurred via (17) and did not produce (19).

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) ($\phi =$ 0.501) was 2.5 times greater than that of cyclohexanone ($\phi =$ 0.20)15 and 6.0 times greater than that of 3-methylcyclohexanone ($\phi = 0.083$).¹³ The rate constant of photolysis of (1) (2.53) \times 10⁸ s⁻¹) was 7.7 times greater than that of cyclohexanone $(0.33 \times 10^8 \text{ s}^{-1})^{13}$ and 10.1 times greater than that of 3-methylcyclohexan-1-one $(0.25 \times 10^8 \text{ s}^{-1})$.¹³ Likewise, quantum yields and rate constants of photolysis of B-trimethylsilyl ketones (7) and (11) were also greater than those of 2-methylcyclohexan-1-one (see Table 2). Introduction of a β-Me₃Si 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 Me₃Si group at the β -position in cycloalkanones provided a regioselective



(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 Me₃Si moiety was not eliminated from diradical intermediates. This observation is in agreement with previous results obtained by others^{3–5} and us:¹² Me₃Si[•] 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 Me₃Si moiety was perfectly aligned for elimination to form a conjugated diene (19), via a diradical

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[‡] For (16): ¹H NMR (CDCl₃, 80 MHz) δ 0.00 (s, 9H, SiMe₃), 1.62–1.73 (m, 1H, HCSiMe₃), 1.91–1.99 (m, 2H, CH₂C=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.

| Ketone | Quantum yield (\$\phi\$)ª | Quantum yield ratio | Reaction rate $(1/\tau \times 10^8 \text{s}^{-1})$ | 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 3-Methylcyclohexan-1-one (22) ^b | 0.20 0.083 | | 0.33 0.25 | |
| (7) 2-Methylcyclohexanone (23) ^b | 0.545 | (7) /(23) = 1.1 | 6.90 4.7 | (7)/(23) = 1.5 |
| (11) | 0.592 | (11)/(23) = 1.2 | 37.9 | (11)/(23) = 8.1 |

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

^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 Me₃SiC–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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