Influence of β-Silyl Groups in Cycloalkanones on the Norrish Type I and Type II Cleavages

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The Norrish type I cleavage overwhelms the type II cleavage in the photolysis of α-alkylcycloalkanones bearing an $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, or $SiPh_3$ group at the β position, of which the quantum yields are often greater than those of the non-silylated cycloalkanones.

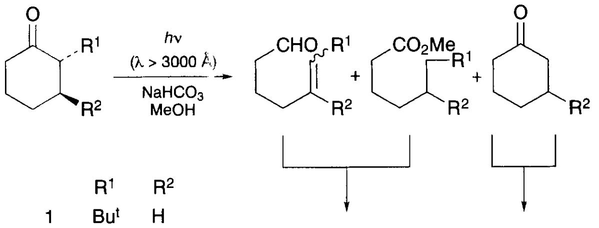
The Norrish type I cleavage provides a valuable tool in organic synthesis[1] and a photochemical pathway to degrade carbonyl compounds.[2] The Norrish type II cleavage usually prevails over the type I cleavage during the photolysis of cycloalkanones bearing a γ hydrogen on an α side chain. Examples include the photolysis of α-alkylcyclohexanones **1–3**,[3] from which the ratios of products are 0.3–1. for type I/type II. To intensify the type I cleavage and ultimately to force it to be the major pathway, we searched for a special moiety that can stabilize the radical intermediate generated in the type I process.

Use of a β-$SiMe_3$ group to direct the Norrish type I cleavage of cycloalkanones was first reported in early 1990.[4] This new reaction was soon applied in organic synthesis.[5–8] Herein we report our new findings that various organosilyl groups can promote Norrish type I cleavage to occur as the major pathway in cycloalkanones bearing a γ hydrogen on an α side chain.

α-Alkyl-β-(trimethylsilyl)cyclohexanones **4a–6a** (*cf.* the corresponding non-silylated cycloalkanones **1–3**[3]) possess a primary, secondary, and tertiary γ hydrogen, respectively. We irradiated these cycloalkanones in anhydrous methanol containing 1.3 equiv. of $NaHCO_3$ with UV light (λ > 3000 Å). Distribution of the type I products, including aldehydes **4b–6b** and esters **4c–6c**, and the type II product **16** is summarized in Scheme 1 and Table 1 (entries 4–6). In all of these reactions, the major products came from type I cleavage (type I/type II = 2.1–4.9). We also found that the quantum yields[9] for β-silylated cycloalkanones were always greater than those of the corresponding non-silylated cycloalkanones (see Table 1). We then attached various silyl groups, including $SiMe_2Ph$, $SiMePh_2$, and $SiPh_3$, onto α-alkylcycloalkanones. The major products obtained by irradiation of those silylcycloalkanones **7a–15a** came from type I cleavage (Table 1).

Our results indicate that organosilyl groups presented a different influence on the product distribution from type I and type II cleavages. All of the four groups, $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$ and $SiPh_3$, at the β position in α-alkylcycloalkanones were able to force type I cleavage to be the major photolytic pathway regardless of the γ hydrogen on the α side chain being primary, secondary, or tertiary (Table 1, third column, entries 4–15). The highest ratio for type I/type II was 9.7, which was obtained by use of the $SiMePh_2$ group (entry 11). In comparison with the ratio of 0.5 in the photolysis of the corresponding non-silylated cyclohexanone **2** (entry 2), the influence from the $SiMePh_2$ group was ≈20 fold.

We found that the quantum yields for cyclohexanones bearing a β-$SiMe_3$, -$SiMe_2Ph$, or -$SiMePh_2$ group were 1.3–8.9 times higher than those of the non-silylated cycloalkanones (Table 1, entries 4–12). Among those silyl groups, $SiMe_2Ph$ showed the most remarkable effect (entry 8). Our results in Table 1 revealed that, in comparison with the $SiMe_3$ group, a silicon atom attached with a phenyl group often exhibited greater influence on quantum yields of Norrish type cleavages.

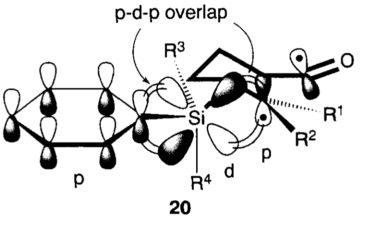


	R^1	R^2	Type I products (isolated % yield)				Type II products (isolated % yield)	
1	Bu^t	H						
2	Pr^n	H						
3	Bu^i	H						
4a	Bu^t	$SiMe_3$	**4b**	(10)	**4c**	(62)	**16**	(23)
5a	Pr^n	$SiMe_3$	**5b**	(30)	**5c**	(50)	**16**	(17)
6a	Bu^i	$SiMe_3$	**6b**	(30)	**6c**	(32)	**16**	(29)
7a	Bu^t	$SiMe_2Ph$	**7b**	(5)	**7c**	(49)	**17**	(15)
8a	Pr^n	$SiMe_2Ph$	**8b**	(20)	**8c**	(39)	**17**	(13)
9a	Bu^i	$SiMe_2Ph$	**9b**	(18)	**9c**	(29)	**17**	(29)
10a	Bu^t	$SiMePh_2$	**10b**	(9)	**10c**	(47)	**18**	(26)
11a	Pr^n	$SiMePh_2$	**11b**	(18)	**11c**	(50)	**18**	(7)
12a	Bu^i	$SiMePh_2$	**12b**	(19)	**12c**	(34)	**18**	(25)
13a	Bu^t	$SiPh_3$	**13b**	(0)	**13c**	(70)	**19**	(20)
14a	Pr^n	$SiPh_3$	**14b**	(0)	**14c**	(55)	**19**	(16)
15a	Bu^i	$SiPh_3$	**15b**	(8)	**15c**	(22)	**19**	(27)

Scheme 1 Photolysis of β-silylcyclohexanones to give a mixture of products from the Norrish type I and type II processes

Table 1 Comparison of the product distributions and quantum yields (Φ) in the photolysis of β-silylated and non-silylated cyclohexanones through the Norrish type I and type II cleavages

Entry	Cycloalkanone	Product ratio Type I/Type II	Quantum yield (Φ)	Φ_{Si}/Φ_{parent}
1	**1**	1.0	0.120	—
2	**2**	0.5	0.082	—
3	**3**	0.3	0.070	—
4	**4a**	3.1	0.151	1.3
5	**5a**	4.9	0.124	1.5
6	**6a**	2.1	0.106	1.5
7	**7a**	3.6	0.464	3.9
8	**8a**	4.5	0.728	8.9
9	**9a**	1.6	0.390	5.6
10	**10a**	2.2	0.258	2.2
11	**11a**	9.7	0.246	3.0
12	**12a**	2.1	0.118	1.7
13	**13a**	3.6	0.041	0.34
14	**14a**	3.7	0.068	0.83
15	**15a**	1.1	0.165	2.4



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A silyl group can stabilize a β-carboradical through 'σ–π hyperconjugation'[10–13] or 'p–d homoconjugation'[14,15] or both. We believe that the p orbitals in the phenyl group could enhance 'p–d homoconjugation' resulting from the silicon atom by offering 'p–d–p homoconjugation' to stabilize the β-carboradical. Structure **20** depicts the 'p–d–p' orbital overlap among a phenyl ring, a silicon atom, and a carboradical.

This work was supported by the National Science Council of Republic of China (Grant NSC 84-2113-M007-004) and Academia Sinica.

Received, 8th November 1994; Com. 4/06808D

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