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The Operation of H-Atom and TMS-Group Transfer Processes in the Photochemistry of Silylamidoalkyl- and Silylalkyl-Ketones and -Phthalimides

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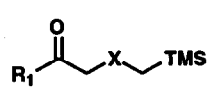
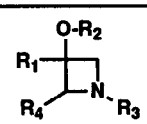
Abstract. Photoreactions of silylamidoalkyl- and silylalkyl-ketones and N-silylethylphthalimide operate by competitive H-atom and TMS-group transfer routes and whose relative efficiencies are influenced by side-chain and carbonyl substituents, and solvent.

Two major reaction pathways, the Norrish Type I and Type II processes, characterize the excited state chemistry of carbonyl compounds.[1] The Type II reaction, involving predominantly γ-H atom abstraction, typically occurs from both singlet and triplet excited carbonyls having n-π* (*i.e.* oxy-radical like) electronic configurations. 1,4-Biradicals generated in this way undergo cyclization to yield cycloalkanols and/or fragmentation to give enols and alkenes.

Studies of phthalimides[2] and amino-ketones[3] have shown that Type II photoreactions can also be promoted by charge transfer (CT) between donors and either n-π* or π-π*carbonyl acceptors. Our recent efforts have focused on the SET-photochemistry of silicon-substituted donors.[4] In this communication we describe results of continuing investigations in this area in which we have probed the photochemistry of several trimethylsilyl-methylamido (**1-4**) and -alkyl (**5-6**) ketones and the N-silylethylphthalimide **21** and through which we have uncovered novel Type II-like chemistry, involving either transfer or loss of a TMS group.



	R_1	X
1	phenyl	NCO_2Bn
2	2-naphthyl	NCO_2Bn
3	1-clohexenyl	NCO_2Bn
4	9-phenanthrenyl	NCO_2Bn
5	phenyl	CH_2
6	2-naphthyl	CH_2
7	4-cyanophenyl	CH_2



	R_1	R_2	R_3	R_4
8	phenyl	TMS	CO_2Bn	H
9	phenyl	H	CO_2Bn	H
10	phenyl	H	CO_2Bn	TMS
11	2-naphthyl	TMS	CO_2Bn	H
12	2-naphthyl	H	CO_2Bn	H
13	2-naphthyl	H	CO_2Bn	TMS
14	1-cyclohexenyl	TMS	CO_2Bn	H
15	9-phenanthrenyl	TMS	COMe	H

Initial indications of interesting chemistry came from our studies with ketones **1-4**. Irradiation (λ > 300 nm) of silylamido-phenone **1** in MeCN leads to formation of a separable (silica) mixture of azetidines **8-10** (see Table 1) along with PhCOMe (6%) and the carbamate **16** (6%). NMR analysis shows that azetidinol **9** is absent from the crude photolysate and, thus, that **9** comes from **8** during chromatography. In addition, the naphthyl-analog **2** is transformed in

nearly equal efficiency by irradiation in MeCN to azetidines **11-13** (Table 1), 2-acetonaphthone (14%) and carbamate **16** (5%). Finally, the siloxyazetidines **14** and **15** are the major products from respective photoreactions of the cyclohexenyl- and 9-phenanthrenyl-ketones, **3** and **4**.[5] *The above observations show that the major route followed in the photoreactions of these silylamido-ketones involves TMS-group transfer to the carbonyl oxygen followed by diradical coupling.*[6]

Table 1. Azetidine Products and Yields from Direct Irradiations of Silylamido-Ketones **1-4** in MeCN.

Starting Ketone	Azetidines (Isolated Yield) ((NMR-Yield))[a]
1	**8** (22%) ((29%)), **9** (13%), **10** (9%) ((18%))
2	**11** (6%) ((37%)), **12** (15%), **13** (1%) ((5%))
3	**14** (36%)
4	**15** (*ca.* 50%)

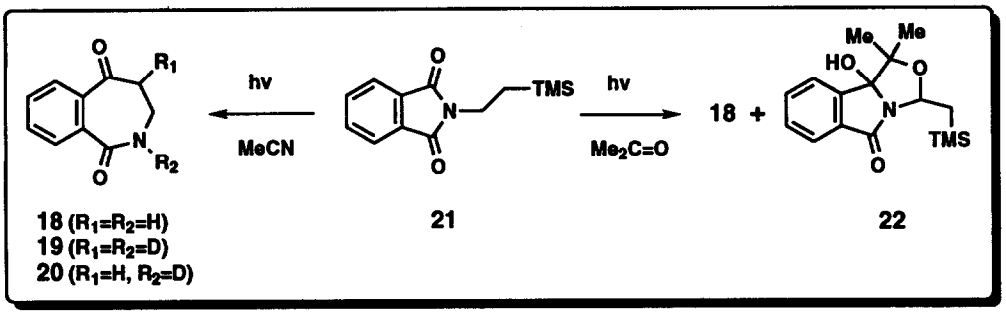
([a]) ^{1}H NMR analysis of crude photolysates from irradiations in CD_3CN.

The TMS-propyl ketones **5**[7] and **6** both undergo clean photoreactions (but with different efficiencies, **5** > **6**) in MeCN to produce the corresponding methylketones (ArCOMe) and vinylsilane (H_2C=CHTMS) in near equal yields (80-100%) along with the diketones ($ArCOCH_2CH_2COAr$, 10-19%). The photochemistry of the p-cyano analog **7** in MeCN is a bit more complex, giving 4-CN-$C_6H_4COCH_3$ (91%), H_2C=CHTMS (92%) and (4-CN-$C_6H_4COCH_2)_2$ (1%) and the cyclobutanol **17** (7%). *Thus, in contrast to their silylamide analogs, the silylalkyl ketones react nearly exclusively by H-atom migration pathways in MeCN.*

Observations which connect the two disparate photochemical reactivity patterns have come from ^{1}H NMR monitoring of the photoreactions of **5** and **7** in CD_3CN and CD_3OH. Low conversion (*ca.* 5-20%) irradiation of both **5** and **7** in CD_3CN leads to formation of ArCOMe and H_2C=CHTMS products in 1:1 ratios. However, irradiation of **5** in CD_3OH again gives the ketone and vinylsilane, but this time in a 1.7:1 ratio. Also, photoreaction of the 4-cyano compound **7** in CD_3OH gives methyl ketone and vinylsilane in a ratio of 1.8:1. The corresponding silylenol ethers, $ArC(OTMS)=CH_2$, were not detected in the crude CD_3OH photolysates despite the fact that they are stable under the reaction conditions. *Clearly, two pathways are followed in the excited reactions of 5 and 7 in CD_3OH, one involving H-*

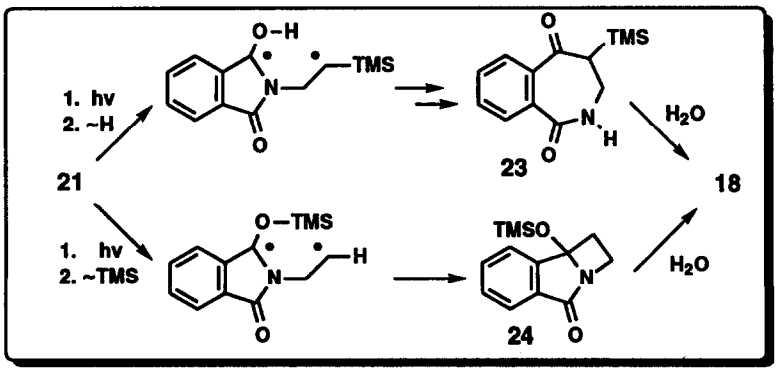
atom migration to produce methyl ketone and vinylsilane in equal amounts and the other involving desilylation to give the methyl ketone (and CH_2=CH_2 presumably) and no vinylsilane.

The generality of these observations is reflected in the photochemistry of the silylethylphthalimide **21**. Irradiation (λ > 250 nm) of **21** in MeCN (*ca.* 1 mM) followed by silica gel chromatography leads to the known[8] benzazepindione **18** (68%). This substance (41%) along with the TMS-containing adduct **22** (7%) are formed when **21** is irradiated in acetone.



While, precedence exists for formation of adduct **22** by acetone trapping of an ylid intermediate derived by H-atom migration,[9] the mechanism(s) for production of benzazepindione **18** is less clear. Two limiting routes are reasonable. One involves typical γ-H-atom abstraction followed by diradical cyclization and amidol ring opening to give the α-silylketone **23** (Scheme 1). Exposure of **23** to water then provides **18**. Alternatively, TMS-group migration to oxygen in excited **21** would generate the tricyclic silyl ether **24**, a substance which should rapidly transform to **1** with water. This mechanistic issue has been clarified. Firstly, as originally observed by Kanaoka,[8] irradiation of N-ethylphthalimide under conditions that promote efficient photoreaction of **21** leads to inefficient (<2%) formation of **18**. Secondly, NMR monitoring of the photoreaction of **21** demonstrates that the α-silylketone **23**[10] is formed in anhydrous CD_3CN. Quenching of this photolysate with D_2O leads to generation of the α-CD,ND-d_2-benzazepindione **19**. On the other hand, Irradiation of **21** in 50% D_2O-CD_3CN gives the ND-d_1-benzazepindione **20** exclusively. *These results shows that 21 gives 18 by a typical H-atom abstraction pathway in MeCN and by a silyl transfer or desilylation route in the more polar/silophilic H_2O-MeCN.*

Scheme 1.



This study has provided a preliminary view of the types of excited state reactions that are open to TMS-substituted ketones and phthalimides and how they are governed by solvent and substituents. In summary, photoreactions of the silylamido-ketones in MeCN appear to occur *via* CT-excited states in which intramolecular migration of the TMS moiety is favored by the high silophilicity of the oxygen of the phenone radical anion in aprotic media. H-Atom abstraction by the carbonyl n-π^* excited state is the dominant process in silylalkyl ketone photochemistry occurring in the less polar solvent MeCN. However, in the more polar MeOH, CT-interactions in the excited states (both π-π^* and n-π^*) of these substances compete and lead to generation of diradicals by MeOH induced desilylation. Finally, CT-interaction in the excited state of the phthalimide **21** enhances silyl transfer or desilylation depending on the silophilicity (H_2O>MeCN) of the solvent. Inherent in this overview are questions about the mechanistic generalities and synthetic implications of the chemistry, issues which future studies will address.

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(10) Characteristic NMR data for **6** are ^{1}H NMR 3.01 pm (1H, dd, J = 12, 4 Hz, O=C-CH-TMS), 3.33 ppm (1H, ddd, J = 15, 7, 4 Hz, N-CH_2), 3.53 ppm (1H, ddd, J = 15, 12, 7 Hz, N-CH_2); ^{13}C NMR 39.5 (NCH_2), 54.3 (CH-TMS).

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