A Novel Fragmentation Reaction of α-(*N*-Siloxy)anilino Ketones induced by Fluoride Ions

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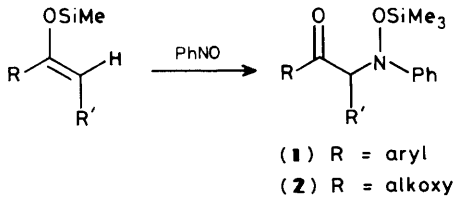
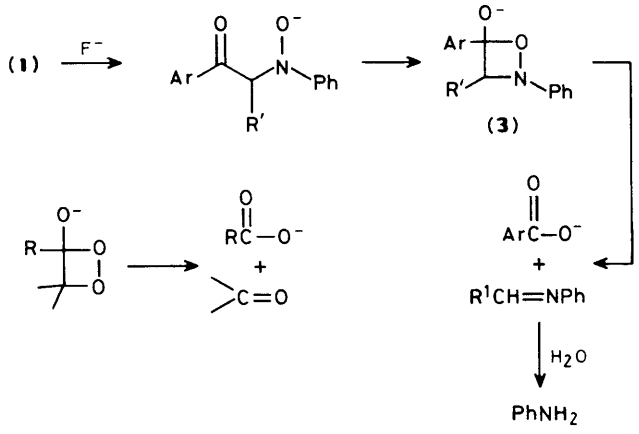
The reaction of α-(*N*-siloxy)anilino-substituted aromatic ketones with tetrabutylammonium fluoride afforded aromatic acids and aniline as the fragmentation products, presumably *via* ring rupture of the intermediate 1,2-oxazetidine.

We have previously reported the facile syntheses of α-(*N*-siloxy)anilino ketones (**1**) and esters (**2**) from the electrophilic addition reactions of nitrosobenzene to silyl enol ethers and silyl ketene acetals.[1] Since this class of compounds is rarely used in syntheses, several reactions have been carried out including elimination to phenylglyoxal anil,[2] oxidation to aroylnitrones,[3] reduction to amino alcohols,[4] and cyclization to isoxazolidine-4,5-dione.[5] We now report the unusual fragmentation of (**1**) induced by fluoride ions. The N–O$^-$ compound was generated by fluoride ion attack on the



Scheme 1



Scheme 2

siloxyamino function, and thereby, fragmented products were obtained; when (**1a**) was treated with tetrabutylammonium fluoride in tetrahydrofuran (THF) at room temperature, benzoic acid (80%) and aniline (35%) were isolated as the acidic and basic fractions after extraction of the products. This fragmentation was observed at a lower temperature (−78 °C). Likewise the other aromatic ketones (**1b—f**) afforded the corresponding acids together with aniline (Table 1). However, the siloxyamino ester (**2**) underwent only desilylation to the free hydroxylamine.

A reasonable explanation for the formation of the fragmented products is shown in Scheme 2; fluoride ion causes desilylation to form selectively an oxygen anion of the hydroxyamino group,[6] and intramolecular nucleophilic addition of the anion thus formed to a carbonyl group may give the key 1,2-oxazetidine intermediate (**3**).[7] Ring rupture would then lead to the formation of two heterounsaturated bonds, namely, a carboxylic acid and an imine hydrolysable to aniline. The formal mode of this fragmentation corresponds to

Table 1. Fluoride ion induced fragmentation of (**1**).

(1)	R (Ar)	R′	Product yield ($ArCO_2H/PhNH_2$, %)
a	Ph	H	80/53 (80/35)[a]
b	Ph	Me	62/21
c	4-ClC_6H_4	H	30/21
d	4-$MeOC_6H_4$	H	41/22
e	1-Naphthyl	H	72/25
f	2-Thienyl	H	32/11

[a] At −78 °C for 5 h (room temperature in parentheses). The isolated yield of aniline was much lower than that of the acid, probably owing to loss by polymerization of the primarily formed imine.

that of the well known dioxetane,[8] and is closely related to that reported for the reaction of an enolate anion with molecular oxygen.[9] The less reactive ester carbonyl group in (**2**) might lead only to desilylation at the first stage.

The same fragmentation pattern was also found in the reaction of the lithium enolate of acetophenone, generated with lithium di-isopropylamide, with nitrosobenzene at −78 °C, followed by treatment with acid, to give directly benzoic acid in 32% yield possibly *via* the same intermediate (**3**). Further detailed studies on the intermediate are in progress including the question of chemiluminescence.

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References

1 T. Sasaki, Y. Ishibashi, and M. Ohno, *J. Chem. Res.*, 1984, (**5**), 218; (*M*), 1972.
2 T. Sasaki, Y. Ishibashi, and M. Ohno, *Chem. Lett.*, 1983, 863.
3 T. Sasaki, K. Mori, and M. Ohno, *Synthesis*, 1985, 279.
4 T. Sasaki, K. Mori, and M. Ohno, *Synthesis*, 1985, 280.
5 M. Ohno, K. Mori, M. Ido, and S. Eguchi, *Synthesis*, 1986, 666.
6 E. Colvin, 'Silicon in Organic Synthesis,' Butterworths, London, 1981.
7 A few reports on 1,2-oxazetidine derivatives indicated that the ring is cleaved consistently across the N–O bond; J. W. Timberlake and E. S. Elder, in 'Comprehensive Heterocyclic Chemistry,' eds. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984, vol. 7, p. 457.
8 W. Adam, in 'The Chemistry of Peroxides,' ed. S. Patai, Wiley, Chichester, 1983, ch. 24; in 'Chemical and Biological Generation of Excited States' eds. W. Adam and G. Cilento, Academic Press, New York, 1982, ch. 4.
9 I. Kamiya and T. Sugimoto, *Chem. Lett.*, 1976, 33.