

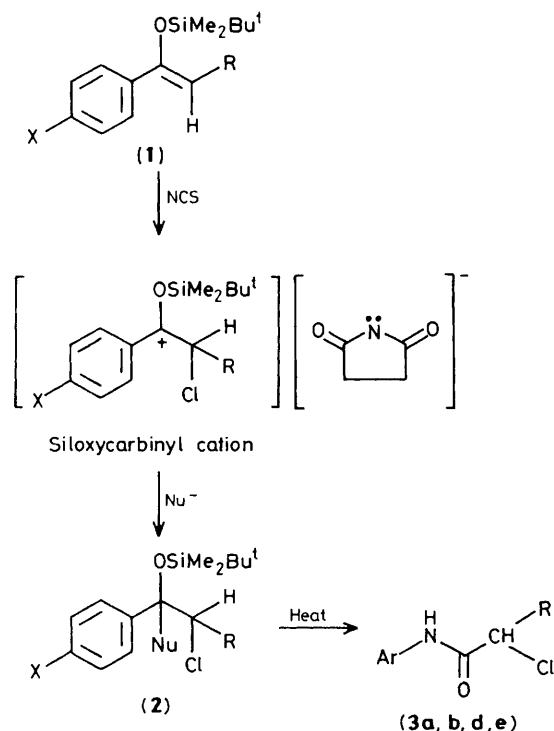
Reaction of Silyl Enol Ethers with *N*-Chlorosuccinimide: Trapping of the Siloxycarbonyl Cation by an Azide Anion

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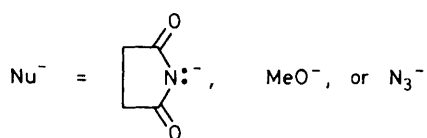
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Reaction of silyl enol ethers (**1a–f**) with *N*-chlorosuccinimide afforded siloxycarbonyl cations which were trapped by nucleophiles (NaN₃ and MeOH); subsequent rearrangement of the azido products (**2a,b,d,e–N₃**) under reflux in decalin led to anilide derivatives (**3a,b,d,e**).

Recently, Chan and his co-worker proposed that a number of trimethylsilyl enol ethers reacted with *N*-chlorosuccinimide (NCS) via a stepwise process involving a silicon-containing intermediate.¹ The same kind of intermediate has been assumed to occur in acid-catalysed equilibration between regioisomers of silyl enol ethers.^{2a†} In both cases, however,



- a**; X = MeO, R = H
b; X = Me, R = H
c; X = H, R = H
d; X = H, R = Me
e; X = H, R = PhCH₂CH₂



Scheme 1

† We have found that 2-*t*-butyldimethylsilyloxy-3-methylbut-1-ene (a kinetically controlled silyl enol ether) was smoothly isomerized into 2-*t*-butyldimethylsilyloxy-3-methylbut-2-ene (thermodynamically controlled) in the presence of pyridinium hydrochloride in chloroform solution.^{2b}

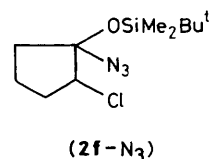
attempts to trap an intermediate using nucleophiles have been unsuccessful. Interest in the mechanism of generation of siloxycarbonyl cations and the possibility of new synthetic applications of silyl enol ethers led us to attempt to trap the intermediate by nucleophiles such as methanol and azide ions.

While reaction of (**1a**) with NCS in acetonitrile afforded only the simple adduct (**2a–NCS**, 99% yield) as reported by Chan *et al.*,¹ the reaction carried out in methanol gave the chloro-methoxy derivative (**2a–OMe**, 75% yield). Reaction of (**1a–e**) with NCS in acetonitrile in the presence of NaN₃ and PhCH₂NEt₃⁺Cl⁻‡ afforded chloro-azido derivatives (**2a–e–N₃**) in fair to good yield (see Table 1). An independent control experiment showed that the adduct (**2a–NCS**) is stable under these reaction conditions and also that chloro-azido derivatives could not be obtained in the absence of PhCH₂NEt₃⁺Cl⁻. The siloxycarbonyl cation formed from silyl enol ether (**1f**) of cyclopentanone was also trapped by the azide anion to afford the corresponding azido derivative (**2f–N₃**) along with some minor products (α -chlorocyclopentanone and 3-chloro-2-*t*-butyldimethylsilyloxycyclopentanone), but the simple NCS-adduct was not detected. Structural

Table 1. Trapping of the siloxycarbonyl cation formed from silyl enol ethers (**1a–f**) with *N*-chlorosuccinimide

Product	Nu	Yield/% ^a
(2a–NCS)	Succinimido	99
(2a–OMe)	MeO	75
(2a–N₃)	N ₃	61
(2b–N₃)	N ₃	78
(2c–N₃)	N ₃	33
(2d–N₃)	N ₃	58 ^b
(2e–N₃)	N ₃	48 ^b
(2f–N₃)	N ₃	47

^a Isolated by t.l.c. on silica gel (hexane–ether eluant). ^b Diastereoisomeric mixture (*ca.* 3:1).



‡ General procedure: To a mixture of silyl enol ether (**1a**) (0.91 mmol), benzytriethylammonium chloride (1.3 mmol), and sodium azide (2.0 mmol), in MeCN (10 ml), was added a solution of NCS (2.0 mmol) in the same solvent (5 ml). The resulting mixture was stirred for 2 h at room temp. before quenching with water. The product was extracted into dichloromethane and dried with sodium sulphate, removal of solvent gave a yellow oil. T.l.c. silica gel (hexane–ether eluant, 5:1) gave (**2a–N₃**) (61% yield).

assignment of (**2a**-N₃) was based on spectral data and its rearrangement reactions. The i.r. spectrum of (**2a**-N₃) featured the azido band at 2125 cm⁻¹ and the ¹H n.m.r. spectrum showed the CH₂ protons as an AB quartet (*J* 10 Hz) at δ 3.70 and 3.83 in CDCl₃ influenced by the neighbouring asymmetric carbon. § Satisfactory spectra were also obtained for the other products (**2b**-f-N₃).

From these results, it is clear that the siloxycarbonyl cation is formed during the reaction and that it has considerable stability in solvent-free form.

§ *Spectral data.* (**2a**-N₃): ¹H n.m.r. (CDCl₃) δ 0.08 (s, 3H), 0.26 (s, 3H), 1.00 (s, 9H), 3.70, 3.83 (ABq, *J* 10 Hz, 2H), 3.80 (s, 3H), 6.90 (d, *J* 10 Hz, 2H), 7.43 (d, *J* 10 Hz, 2H); i.r. 2970, 2125, 1520, 1265, 840 cm⁻¹; *m/z* 328, 326 (*M*⁺ - 15), 315, 313 (*M*⁺ - 28), 301, 299 (*M*⁺ - 42), 286, 284 (*M*⁺ - 57).

(**3a**): ¹H n.m.r. (CDCl₃) δ 3.79 (s, 3H), 4.15 (s, 2H), 6.86 (d, *J* 9.0 Hz, 2H), 7.42 (d, *J* 9.0 Hz, 2H), 7.76-8.31 (bs, 1H); *m/z* 201, 199 (*M*⁺), 124, 122 (*M*⁺ - 77).

Finally, heating of chloro-azido derivatives (**2a**, **b**, **d**, **e**-N₃) in boiling decalin produced the respective anilide derivatives (**3a**, 45%; **3b**, 99%; **3d**, 65%; **3e**, 62% yield) *via* Schmidt type rearrangements. § This transformation sequence can be regarded as a synthetic method for conversion of acylbenzenes into anilides in the absence of any acid catalyst.³

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References

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- 2 (a) G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, 1968, **90**, 4462; (b) K-y Akiba *et al.*, unpublished results.
- 3 *E.g.* Synthesis of analogous siloxyazides has been achieved by addition of Me₃SiN₃ to aldehydes; see L. Birkofer and W. Kaiser, *Liebigs Ann. Chem.*, 1975, 266.