Silylhydroxylamines as Reagents for High-yield RCOCl → RNCO Conversions

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Summary Silylated hydroxamic acids, $RCON(OSiMe_3)SiMe_3$, readily prepared from acid chlorides and $Me_3SiONHSiMe_3$ or $Me_3SiON(SiMe_3)_2$, fragment at 410—430 K to give the corresponding isocyanates, RNCO, in high yield.

COMPOUNDS of type (**1**) are known to decompose upon heating to give low-valent species such as carbenes[1] (M = C,

$$R^1_nM(OR^2)SiMe_3 \rightarrow R^1_nM: + Me_3SiOR^2$$

(**1**)

$n = 2$), silylenes[2] (M = Si, $n = 2$), and nitrenes[3] (M = N, $n = 1$). We now describe a preparatively useful example of the latter which is reminiscent of the Lössen rearrangement.[4]

Treatment of acid chlorides with (i) $Me_3SiONHSiMe_3$[5] and Et_3N, (ii) $Me_3SiONLiSiMe_3$† or, *most usefully*, (iii) $Me_3SiON(SiMe_3)_2$[5] results in good yields (> 75%) of silylated hydroxamic acids,‡ $RCON(OSiMe_3)SiMe_3$ (**2**), which, if required, may be isolated by low-pressure distillation. At 410—430 K, in an inert solvent such as mesitylene, compounds (**2**) fragment cleanly and rapidly to give $(Me_3Si)_2O$ together with the corresponding isocyanate,§ RNCO, in virtually quantitative yields, as shown in the Scheme.

Each of the initial steps has its particular merit; for example, (ii) is useful for low-boiling acid chlorides: conversion of propioloyl chloride in this context provides a means for the first authentic synthesis of isocyanatoethyne.¶

$$\begin{tikzcd}
RCOCl \arrow[r, "(i), (ii), or (iii)"] & RCON(OSiMe_3)SiMe_3 \arrow[d, "410—430\ K"] \\
RNCO & {[RCON:] + (Me_3Si)_2O} \arrow[l]
\end{tikzcd}$$

SCHEME

(i) $Me_3SiONHSiMe_3 + Et_3N$ (excess), light petroleum (b.p. 40—60 °C), 2 h, 293 K, R = Me, Bu^t, XC_6H_4 (X = *m*- or *p*-OMe, *p*-Me, or *p*-NO_2); (ii) $Me_3SiONLiSiMe_3$, ether, 233 K, 15 min, R = HC≡C; (iii) $Me_3SiON(SiMe_3)$, mesitylene, 353 K, 30 min (Me_3SiCl is distilled continuously from the reaction mixture), R = Ph or *E*-PhCH=CH.

Method (iii) is attractive in that the whole sequence: RCOCl → $RCON(OSiMe_3)SiMe_3$ → RNCO can be carried out in homogeneous solution without interruption. However, until $Me_3SiONHSiMe_3$ and $Me_3SiON(SiMe_3)_2$ become available commercially, method (i) may be preferred because $Me_3SiONHSiMe_3$ is prepared directly from Me_3SiCl and hydroxylamine,[5] whereas the synthesis of $Me_3SiON(SiMe_3)_2$ requires a further metallation step.[5]

The conversion applies equally well to the analogous sulphur compounds; thus treatment of PhCSCl with $Me_3SiON(SiMe_3)_2$ gives, initially, $PhCSN(OSiMe_3)SiMe_3$, which upon thermolysis gives the isothiocyanate, PhNCS, in high yield.

The decomposition of $PhCON(OSiMe_3)SiMe_3$ in mesitylene in the 383—433 K range is cleanly first order with respect to

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† The low temperature *must* be maintained during the coupling step, otherwise $Me_3SiONLiSiMe_3$ rearranges to $(Me_3Si)_2NOLi$ resulting in $RCO_2N(SiMe_3)_2$ products; see R. West, P. Boudjouk, and A. Matuszko, *J. Amer. Chem. Soc.*, 1969, **91**, 5184.

‡ If desired, the free hydroxamic acids, RCONHOH, may be liberated quantitatively by treating the silylated species (**2**) with MeOH at room temperature.

§ All compounds were characterised by standard analytical and spectroscopic techniques [notably ν(NCO), *ca.* 2260 cm^{-1}].

¶ Experiments by Mr. T. Cooper: a preliminary microwave spectral analysis shows the unstable product, HC≡CNCO to be a planar V-shaped molecule with ∠CNC = *ca.* 150°.

substrate up to *ca.* 80% of reaction and the derived thermodynamic parameters, $\Delta H^{\ddagger}$ 138 kJ mol^{-1}, $\Delta S^{\ddagger}$ -9 J K^{-1} mol^{-1}, are close to those determined for the thermolysis of PhN(OSiMe$_3$)SiMe$_3$,[3] *viz.* $\Delta H^{\ddagger}$ 116 kJ mol^{-1}, $\Delta S^{\ddagger}$ -16 J K^{-1} mol^{-1}.

Preliminary trapping experiments designed to establish the intermediacy or otherwise of an aroylnitrene as an initial fragmentation product were somewhat inconclusive. Thus heating PhCON(OSiMe$_3$)SiMe$_3$ for 6 h at 355 K in cyclohexene (ten-fold excess) gave PhCONH$_2$ (5—10%), PhNCO [*ca.* 80% conversion based upon the quantity (50%) of substrate decomposed], a small amount of unidentifiable polymer, but no aziridines, such as were isolated, albeit in low yield (2%), in the decomposition of PhN(OSiMe$_3$)-SiMe$_3$.[3] It is noteworthy that thermolysis of Bu^{t}CON$_3$ (Curtius reaction) in an excess of cyclohexene gave exclusively Bu^{t}NCO (100%) although in this instance, photolysis experiments yielded rearranged adducts of cyclohexene, commensurate with nitrene formation.[6]

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