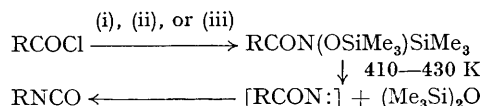


Silylhydroxylamines as Reagents for High-yield RCOCl → RNCO Conversions

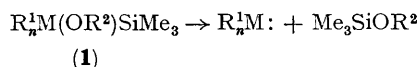
By FRANK D. KING,* STEPHEN PIKE, and DAVID R. M. WALTON*
(School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ)

Summary Silylated hydroxamic acids, RCON(OSiMe₃)-SiMe₃, readily prepared from acid chlorides and Me₃-SiONHSiMe₃ or Me₃SiON(SiMe₃)₂, fragment at 410–430 K to give the corresponding isocyanates, RNCO, in high yield.



SCHEME

COMPOUNDS of type (1) are known to decompose upon heating to give low-valent species such as carbenes¹ (M = C,



$n = 2$), silylenes² (M = Si, $n = 2$), and nitrenes³ (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) Me₃SiONHSiMe₃⁵ and Et₃N, (ii) Me₃SiONLiSiMe₃† or, *most usefully*, (iii) Me₃SiON(SiMe₃)₂⁵ results in good yields (> 75%) of silylated hydroxamic acids,‡ RCON(OSiMe₃)SiMe₃ (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 (Me₃Si)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.¶

† The low temperature *must* be maintained during the coupling step, otherwise Me₃SiONLiSiMe₃ rearranges to (Me₃Si)₂NOLi resulting in RCO₂N(SiMe₃)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 $\nu(\text{NCO})$, *ca.* 2260 cm⁻¹].

¶ Experiments by Mr. T. Cooper: a preliminary microwave spectral analysis shows the unstable product, HC≡CNC to be a planar V-shaped molecule with $\angle \text{CNC} = \text{ca. } 150^\circ$.

(i) Me₃SiONHSiMe₃ + Et₃N (excess), light petroleum (b.p. 40–60 °C), 2 h, 293 K, R = Me, Bu^t, XC₆H₄ (X = *m*- or *p*-OMe, *p*-Me, or *p*-NO₂); (ii) Me₃SiONLiSiMe₃, ether, 233 K, 15 min, R = HC≡C; (iii) Me₃SiON(SiMe₃)₂, mesitylene, 353 K, 30 min (Me₃SiCl is distilled continuously from the reaction mixture), R = Ph or *E*-PhCH=CH.

Method (iii) is attractive in that the whole sequence: RCOCl → RCON(OSiMe₃)SiMe₃ → RNCO can be carried out in homogeneous solution without interruption. However, until Me₃SiONHSiMe₃ and Me₃SiON(SiMe₃)₂ become available commercially, method (i) may be preferred because Me₃SiONHSiMe₃ is prepared directly from Me₃SiCl and hydroxylamine,⁵ whereas the synthesis of Me₃SiON(SiMe₃)₂ requires a further metallation step.⁵

The conversion applies equally well to the analogous sulphur compounds; thus treatment of PhCSCl with Me₃SiON(SiMe₃)₂ gives, initially, PhCSN(OSiMe₃)SiMe₃, which upon thermolysis gives the isothiocyanate, PhNCS, in high yield.

The decomposition of PhCON(OSiMe₃)SiMe₃ in mesitylene in the 383–433 K range is cleanly first order with respect to

substrate up to *ca.* 80% of reaction and the derived thermodynamic parameters, ΔH^\ddagger 138 kJ mol⁻¹, ΔS^\ddagger -9 J K⁻¹ mol⁻¹, are close to those determined for the thermolysis of PhN(OSiMe₃)SiMe₃,³ *viz.* ΔH^\ddagger 116 kJ mol⁻¹, ΔS^\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(OSiMe₃)SiMe₃ for 6 h at 355 K in cyclohexene (ten-fold excess) gave PhCONH₂ (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(OSiMe₃)SiMe₃.³ It is noteworthy that thermolysis of Bu^tCON₃ (Curtius reaction) in an excess of cyclohexene gave exclusively Bu^tNCO (100%) although in this instance, photolysis experiments yielded rearranged adducts of cyclohexene, commensurate with nitrene formation.⁶

We thank the S.R.C. for maintenance awards to F.D.K. and S.P.

(Received, 23rd January 1978; Com. 068.)

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³ F. P. Tsui, T. M. Vogel, and G. Zon, *J. Amer. Chem. Soc.*, 1974, **96**, 7144; F. P. Tsui, Y. H. Chang, T. M. Vogel, and G. Zon, *J. Org. Chem.*, 1976, **41**, 3381.

⁴ W. Lössen, *Annalen*, 1877, **186**, 1; C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 2nd edn., Longmans, London, 1969, p. 748.

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