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Efficient, general synthesis of silylketenes *via* an unusual rhodium mediated Wolff rearrangement

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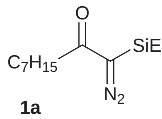
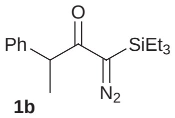
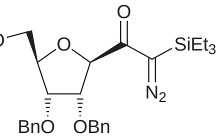
Silylketenes bearing a range of substituents (alkyl, alkenyl, aryl, heteroaryl) are prepared by an unusual rhodium mediated Wolff rearrangement of the corresponding silyl diazo ketones.

Silylketenes are potentially extremely versatile intermediates in organic synthesis.[1] These readily isolable ketenes exhibit extraordinary stability in comparison with their non-silylated counterparts; furthermore, whilst their reactivity shares some common modes with the parent compounds, silylketenes also display a unique and useful chemistry unavailable to their non-silylated counterparts. The development of these compounds as routine synthetic intermediates has been hampered to some extent by the paucity of methods for their preparation in terms of yield and functional group tolerance.[2] We report herein a convenient new high-yielding and general preparation of silylketenes based upon a remarkable rhodium(II) octanoate mediated Wolff rearrangement of silylated diazo ketones.

We have previously disclosed results of our investigations into the chemistry of silylated diazo esters. In particular, we have shown that these compounds undergo intramolecular C–H insertion reactions upon treatment with rhodium(II) carboxylate catalysts in refluxing benzene, giving rise to α-silyl γ-lactones[3] (by insertion into the ester group) or oxasilacyclopentanes[4] (by insertion into ethers attached to the silicon). We were therefore interested in examining the behaviour of silylated diazo ketones under similar conditions. However, upon treatment of 1-diazo-1-(triethylsilyl)nonan-2-one[5] **1a** with rhodium(II) octanoate in benzene at room temperature, a rapid and quantitative (by ^{1}H and ^{13}C NMR) conversion to heptyl(triethylsilyl)ketene **2a** occurred (Scheme 1, Table 1). The ketene could be separated from the rhodium catalyst by chromatography, but the 79% isolated yield of the ketene indicates that some decomposition occurs during purification, possibly through hydration. In order to verify the structure of the ketene, we treated the crude reaction mixture with 1.2 equiv. of $BnNH_2$ in CH_2Cl_2 at room temperature to produce the corresponding α-silyl benzylamide **3a**, which was isolated in 91% yield.


1a


1b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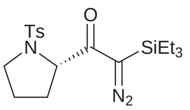
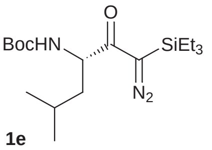
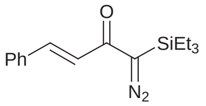
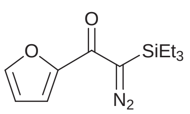
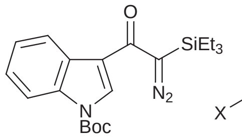
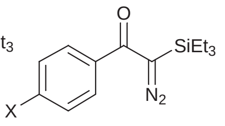

1d


1e


1f


1g

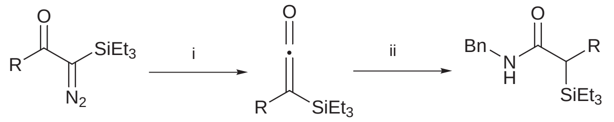

1h


1i X = H
1j X = OMe
1k X = Cl

We next began to examine the functional group tolerance of this new method. As shown in Table 1, the synthesis appears to be general for a range of diazo ketones. The crude reaction mixtures were examined by ^{1}H and ^{13}C NMR to assess the purity of the ketenes prior to isolation by chromatography and/or derivitisation to the stable α-silyl benzylamides. Conversion to the silylketenes was found to be very clean in all cases, with the exception of ketenes **2e**, **2f** and **2i** which contained some minor contaminants. The isolated yields in Table 1 are lower than the observed spectroscopic purities, suggesting that some decomposition (possibly through hydration of the ketene) occurs on chromatography.

Aliphatic substituents are well tolerated (diazo ketones **1a–e**), including those derived from sugars (**1c**) and amino acids (**1d**,**e**). Higher temperatures were required for the decomposition of diazo ketones **1b–e**, possibly reflecting the increased hindrance to attack of the catalyst at the diazo carbon from the branched side-chains. The crude ketene **2e** contained unidentified contaminants which could potentially arise from interception of the intermediate carbenoid by the carbamate protecting group, or by intermolecular N–H insertion.

Alkenyl substituted diazo ketone **1f** furnished ketene **2f** after treatment with the catalyst at 80 °C. This ketene was contaminated with some minor components and was isolated pure in only 33% yield; however the 75% isolated yield of the benzylamine adduct attests to the dominance of the ketene pathway. Heteroaromatic substituents were also tolerated, with

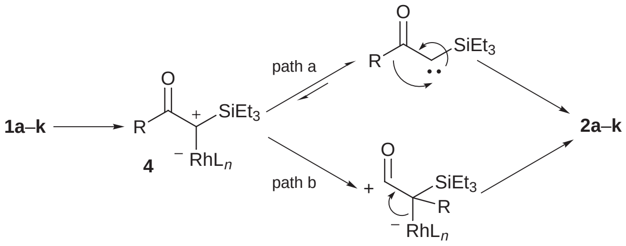

1a–k **2a–k** **3a–k**

Scheme 1 *Reagents and conditions:* i, 1 mol% $Rh_2(O_2CC_7H_{15})_4$, PhH, room temp. to 80 °C; ii, 1.2 equiv. $BnNH_2$, CH_2Cl_2, room temp.

Table 1 Formation of silylketenes by Rh catalysed Wolff rearrangement

Diazo ketone	*T*/°C (*t*/min)	Ketene	Yield (%)[a]	Amide	Yield (%)[b]
1a	20 (10)	**2a**	79	**3a**	91
1b	50 (5)	**2b**	80	**3b**	—[c]
1c	50 (15)	**2c**	41	**3c**	63
1d	80 (30)	**2d**	45	**3d**	0
1e	80 (20)	**2e**	12	**3e**	27
1f	80 (10)	**2f**	33	**3f**	75
1g	60 (30)	**2g**	46	**3g**	87
1h	40 (10)	**2h**	57	**3h**	82
1j	50 (15)	**2i**	54	**3i**	47
1j	20 (5)	**2j**	54	**3j**	60
1k	60 (10)	**2k**	49	**3k**	56

[a] Figures quoted are isolated yields of pure ketene. [b] Yields of amide obtained over two steps from the diazo ketone, without isolation of the ketene. [c] No amide isolated from the reaction with $BnNH_2$.



Scheme 2

2-furyl and indol-3-yl substituted diazo ketones **1g**,**h** rearranging smoothly to the corresponding ketenes **2g**,**h**.

The electronic influence of the diazo ketone substituent upon reactivity is illustrated by the rearrangement of aryl diazo ketones **1i–k**. Decomposition of the phenyl-substituted diazo ketone **1i** occurred at 50 °C to give ketene **2i**. Introducing an electron-releasing *p*-methoxy group to the aromatic ring in diazo ketone **1j** allowed the rearrangement to occur at ambient temperature, while the presence of an electron-withdrawing *p*-chloro group in **1k** required the reaction to be carried out at 60 °C. This order of reactivity could be due to the differing electron density available at the diazo carbon for coordination to the rhodium catalyst, or may reflect the development of a partial positive charge on the migrating group during the rearrangement (*vide infra*). The formation of ketene **2i** was accompanied by some minor by-products which were apparent in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum was not sufficiently resolved to allow an estimation of purity of the crude material, but the 54% isolated yield of the pure ketene reflects a lower limit of the efficiency of the reaction.

Alkyl,[6] aryl[6] and alkenyl[7] substituted silylketenes have previously been prepared from silylated diazo ketones by photolysis, or in a few cases by treatment with copper(I) triflate.[6b] However, the formation of silylketenes from the reaction of silylated diazo ketones with rhodium(II) octanoate is somewhat surprising, since it is a generally held view that the use of rhodium catalysts for diazo ketone decomposition suppresses Wolff rearrangement[8] with only isolated exceptions.[9] That the rhodium(II) octanoate is intimately involved in the rearrangement is supported by the fact that no ketene formation was observed in reactions carried out in the absence of catalyst. We suggest two possible explanations for this anomalous behaviour of silyl diazo ketones. The first is that the silyl group destabilises the putative carbenoid intermediate **4** by the tendency of silicon to destabilise α-positive charges,[10] and also potentially by virtue of its bulk. This leads to decomplexation of the metal (path a, Scheme 2) and subsequent Wolff rearrangement from the free carbene. However, in our studies on silyl diazoacetate decomposition we have seen significant catalyst effects upon the stereochemical outcome of insertion reactions,[3] which argues against a decomplexation of the metal catalyst in this closely related system. We therefore suggest a second mechanism for the rearrangement, based upon the ability of silicon to stabilise β-positive charge.[10] Migration of the diazo ketone substituent in the rhodium carbenoid **4** generates an acyl cation which is stabilised by the β-silyl group (path b, Scheme 2). Loss of the σ-bound rhodium species furnishes the ketene and regenerates the catalyst.

In summary a mild, efficient and functional group tolerant synthesis of silylketenes is presented, proceeding *via* an unusual rhodium mediated Wolff rearrangement. Further investigations of this process, as well as synthetic applications of the silylketenes, are now in hand.

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