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GENERATION OF VINYL CATIONS BY NITROSATION OF *N*-SILYLATED IMINES AND ENAMINES*

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The reaction of monosilylated imines and a disilylated enamine with nitrosyl salts in dichloromethane at −78 °C is shown to proceed via intermediate vinyl diazonium salts and vinyl cations.

INTRODUCTION

Vinyl cations are an important class of carbocations occurring as intermediates in many organic reactions.[1,2] Vinyl cations are generated preferably via solvolytic displacement of vinyl perfluoroalkanesulphonates, by electrophilic addition to alkynes and allenes and photolysis of vinyl halides.[1,2] Sporadic examples of the generation of vinyl cations via vinyl diazonium compounds have been reported in the earlier literature.[3–9]

Recently, the diazotization of mono- and bis-silylated alkyl- and arylamines has been shown to proceed with the formation of the corresponding diazonium salts.[10] The methyldiazonium salts lose nitrogen easily with the formation of derivatives by nucleophilic substitution. This represents a new procedure for diazotation in non-aqueous media under mild conditions.

When this method was applied for the preparation of vinyldiazonium salts, however, the results indicated a complicated reaction mixture and no diazonium compounds were detected.[10] Infrared spectra of the reaction mixture did not reveal any absorption due to a diazo group and nitrogen evolution during the reaction was not observed. It was suggested[10] that the reaction involved a direct attack of nitrosyl cation on the double bond of the substrate giving products through an unknown mechanism.

RESULTS AND DISCUSSION

We have now investigated the reaction of the silylated imines **1** and **2** and the enamine **3** with different nitrosyl salts. *N*-(Trimethylsilyl)-1-phenylethanimine (**1**) and *N*-(trimethylsilyl)-1-phenylpentanimine (**2**) were reacted with nitrosyl salts, NO^+X^- ($X^- = BF_4^-$, $SbCl_5^-$, OTf^-) at −78 °C in dichloromethane to give a mixture of products (Table 1). The formation of phenylacetylene from **1** and 1-phenylpent-1-yne from **2** and **3** strongly supports the intermediacy of vinyl cations via the corresponding vinyldiazonium salt. The products **14** and **15** are obtained as a consequence of the addition of halogen (originating from the respective nitrosyl salts and tetrabutylammonium bromide used) to the triple bond of alkynes formed during the diazotation reaction. The reaction mixtures from **1**–**3** were hydrolysed under neutral conditions [CH_2Cl_2–H_2O (1 : 1), 1 day, room temperature] to give the products shown in Table 1. The ketones **8** and **13** are formed via a secondary reaction during the work-up, in which moisture could not be excluded.

The product composition was found to be dependent on the nitrosyl reagent. The highest alkyne percentage was obtained with nitrosyl tetrafluoroborate. The formation of side-products is favoured with nitrosyl hexachloroantimonate and nitrosyl triflate. The formation of phenylacetylene (**7**) and 1-phenylpent-1-yne (**12**) can be best explained as involving a vinyl diazonium salt, which affords a vinyl cation after loss of nitrogen. There are two logical ways for further reaction of this vinyl cation: proton elimination yielding the corresponding alkynes and addition of nucleophiles. The former route affords compounds **7**

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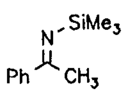
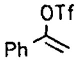
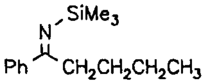
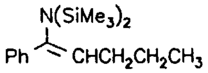
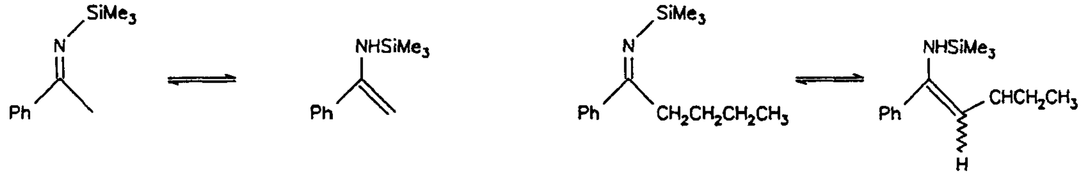
Table 1. Nitrosation of *N*-silylated imines **1** and **2** and enamine **3**[a]

Starting material	Nitrosyl salt	Products			
	$NO^+BF_4^-$	$PhC\equiv CH$	$PhCOCH_3$	$PhC\equiv N$	$PhCOCN$
1	**4**	**7** (14%)	**8** (70%)	**9** (10%)	**10** (6%)
	$NO^+SbCl_6^-$				
	5	**8** (70%)	**10** (6%)		
	NO^+OTf^-				
	6	**7** (34%)	**8** (22%)	**11** (24%)	**1** (8%)
	4	$PhC\equiv CCH_2CH_2CH_3$	$PhCOCH_2CH_2CH_2CH_3$		
		12 (13%)	**13** (18%)		**9** (14%)
		$PhC(Br)=C(Br)CH_2CH_2CH_3$			
		14 (34%)			
	5			$PhC(Cl)=C(Cl)CH_2CH_2CH_3$	
2		**12** (5%)	**13** (15%)	**15** (10%)	
	6	**12** (13%)	**13** (18%)	**2** (2%)	
	**4**	**9** (47%)	**12** (33%)	**13** (7%)	**14** (7%)
	5	**9** (76%)			
3	**6**	**9** (45%)	**12** (28%)		

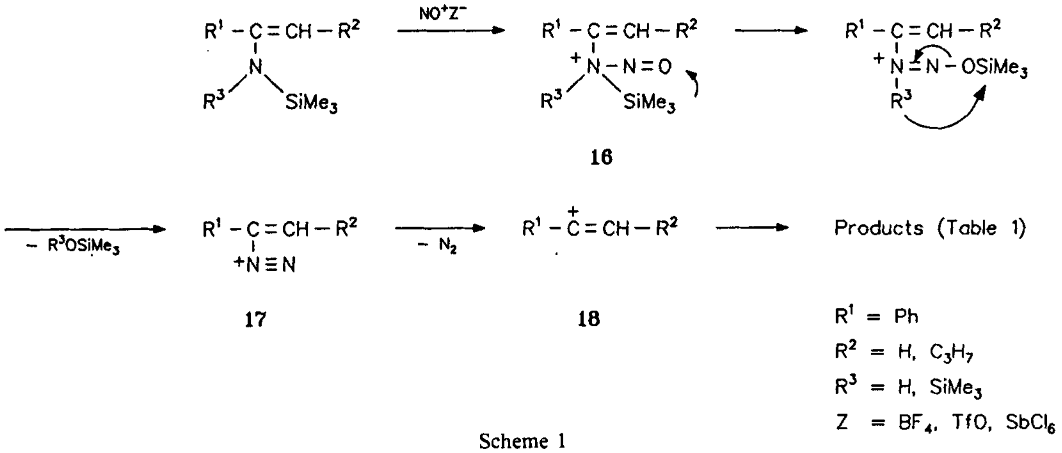
[a] Nitrosation reactions were carried out in CH_2Cl_2 at −78 °C, warmed up to room temperature and quenched with a saturated solution of $Et_4NBr-CH_2Cl_2$. Product compositions were determined by GC–MS and the products were identified by comparison of their properties with those of commercial samples or with samples prepared according to the literature methods. The imine/enamine ratio was determined by NMR and GC:



1 **1a** **2** **2a**

1/**1a** = 94 : 6;[5] **1**/**1a** = 80 : 20 (freshly distilled sample, determined by ^{1}HNMR); **1**/**1a** = 50 : 50 (2-week-old sample, determined by ^{1}HNMR); **2**/**2a**(*z*)/**2a**(*E*) = 52 : 18 : 30;[5] **2**/**2a**(*z*)/**2a**(*E*) = 28 : 60 : 12 (^{1}HNMR); **2**/**2a**(*z*)/**2a**(*E*) = 28 : 54 : 18 (GC).

[b] Only the *E*-isomer is present in the enamine **3**.



Scheme 1

and **12**, whereas the latter gives products **11**, **14** and **15**. The detection of phenylvinyl triflate (**11**) (in the case of nitrosyl triflate as the nitrosyl agent) demonstrates the existence of an intermediate vinyl cation **18** (Scheme 1).

The presence of ketones **8** and **13** in a high ratio is not due to the hydrolysis of the starting silylated imines **1**, **2** and enamine **3**. As mentioned above, compounds **1**–**3** are not hydrolysed under the reaction conditions, but only in the presence of an acidic medium. Moreover, the nitrosyl salts used are very hygroscopic and easily hydrolysable substances. The adventitious moisture present in the reaction medium hinders the diazotization reaction.

We have no satisfactory explanation for the formation of benzonitrile (**9**) and benzoyl cyanide (**10**). However, they could have originated as a consequence of fragmentation of the intermediate **16**, formed by the electrophilic addition of nitrosodium cation to the nitrogen atom.

A general mechanism for the nitrosation of *N*-silylenamines is proposed in Scheme 1. While an equilibrium exists between imine and enamine, as shown by NMR and GC data (see footnote a, Table 1), the proposed mechanism is also valid for *N*-silylated imines. In the first step an *N*-nitrosoammonium salt (**16**) was formed, which through two concerted rearrangements afford the diazonium salt **17**. This salt loses nitrogen easily, yielding the vinyl cation **18**.

CONCLUSIONS

The reaction of monosilylated imines and bis-silylated enamine with nitrosyl salts in aprotic and non-solvolytic media under mild conditions affords products derived from vinyl cations. Further work to generalize the generation of vinyl cations by this method is in progress.

EXPERIMENTAL

Monosilylated imines **1** and **2** and bis-silylated enamine **3** were prepared according to the literature.[11,12] Nitrosyl tetrafluoroborate (Merck) was used without purification. Nitrosyl hexachloroantimonate and nitrosyl triflate were prepared according to the literature.[13]

Nitrosation reaction; general procedure. To a suspension of the appropriate nitrosyl salt (1 mmol) in anhydrous CH_2Cl_2 (5 ml) under an atmosphere of nitrogen at −78 °C was added dropwise the corresponding silylated amine (1 mmol) in anhydrous CH_2Cl_2 (5 ml). The mixture was stirred for 1 h at −78 °C and then brought to room temperature. A saturated solution of tetraethylammonium bromide in CH_2Cl_2 or trifluoroethanol (5 ml) was added and the resulting mixture was stirred for 2 h at room temperature. The solvent was evaporated and the residue was extracted several times with diethyl ether. After filtration, the diethyl ether was removed and the residue was purified by bulb-to-bulb distillation at room temperature (10^{-2} mbar) into a receiver cooled with liquid nitrogen. The distillate was analysed by GC–MS (Table 1).

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