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THE SEARCH FOR THE ETHYNYL CATION: NITROSATION OF *N,N*-BIS(TRIMETHYLSILYL)YNAMINES

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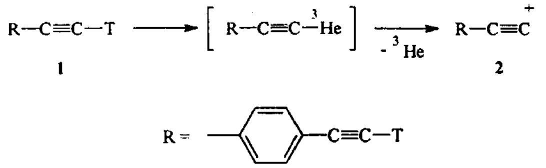
The reaction of bis-silylated ynamines with different nitrosyl reagents affords products derived from an electrophilic attack at the β-carbon atom and not the expected alkynyldiazonium salts.

INTRODUCTION

Ethynyl cation **2** was generated for the first time in 1988 by the β-decay of a tritium substituted alkyne **1** (Scheme 1).[1]



Scheme 1

Ethynyl cations have eluded generation by solvolytic procedures.[2] Other potential precursors for the generation of ethynyl cations are ethynyldiazonium salts. However, theoretical calculations have shown that the unimolecular, thermal dediazoniation of the parent ethynyldiazonium ion is greatly endothermic and kinetically hindered.[3] Ethynyldiazonium salts are not easy to prepare because they are unstable even in non-nucleophilic solvents.[4] The first reported example of a stable diazonium function attached to a sp-hybridized carbon atom was the synthesis of a cyclopropeniumdiazonium salt.[5]

The diazotization of *N*-silylated amines, imines and enamines is a new method for the generation of alkyl,[6] aryl[6] and vinylcations[7] via their corresponding diazonium salts.

RESULTS AND DISCUSSION

We have investigated the reaction of the bis-silylated ynamines **3** with different nitrosyl salts (NO^+X^-, $X = BF_4$, $SbCl_6$, Cl, OTf) at −78 °C in different solvents (CH_2Cl_2, C_6H_6) (Schemes 2 and 3). Tetraethylammonium bromide was used as the trapping reagent when the solvent could not act as the nucleophile itself. Caesium fluoride was used as a catalyst in order to promote the fission of the nitrogen–silicon bond.

The nitrosation of *N,N*-bis(trimethylsilyl)-4-methoxyphenylynamine (**3b**) affords a complicated mixture which could not be resolved. The products of the nitrosation of **3a** could be identified and are summarized in Table 1.

Only in two cases did we detect compounds (**15** and **16**) which may be formulated as follow-up products from an ethynyl cation. A plausible reaction pathway for the formation of **15** and **16** via an ethynyl cation is given in Scheme 4. However, these compounds are formed only in trace amounts, and therefore this mechanism plays either a minor or no role.

Phenylacetonitrile (**6**) is obtained in significant amounts in all reactions. This compound is the prototropic form of the phenylynamine which is the product of the hydrolysis of **3a**, that took place despite efforts to exclude moisture in the reaction medium. This was confirmed independently by hydrolysis of **3a**. Other main products detected are α-hydroxylaminophenylacetonitrile (**7**) and α-*O*-trimethylsilylhydroxylamino-

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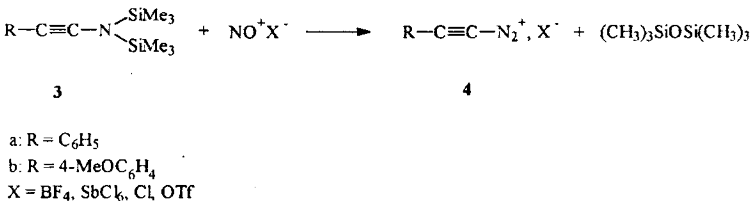
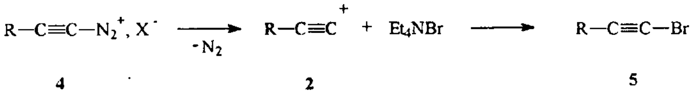
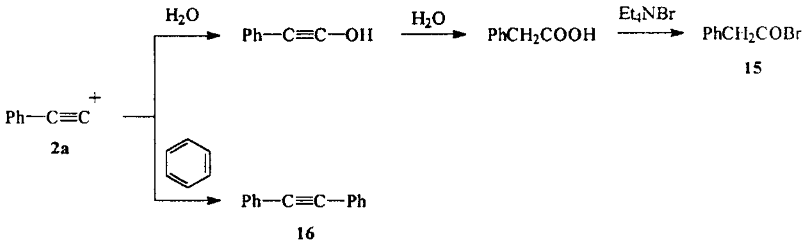


Scheme 2



Scheme 3



Scheme 4

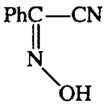
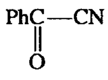
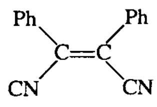
phenylacetonitrile (**14**), formed by attack of the nitrosyl ion at the β-carbon atom of the ynamine **3a** (Scheme 5).

The proposed mechanism is supported by the identification of **14**, which was detected in the reaction mixture. This follows the pattern reported previously in which silylated ynamines were treated with aldehydes[8] or with thionyl chloride.[9] In accordance with these reports, our results show that the β-carbon atom and not the nitrogen atom is the nucleophilic centre.

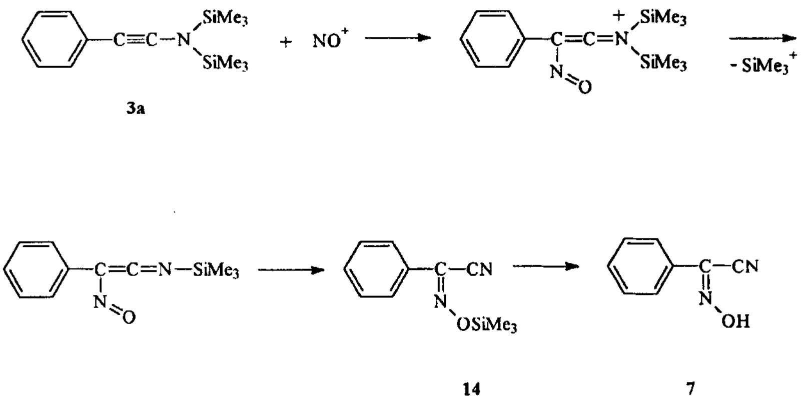
Comparing the results summarized in the Table 1 for the reaction of **3a** with nitrosyl tetrafluoroborate in methylene chloride and benzene, neither the solvent nor the presence of tetraethylammonium bromide appears to influence the distribution of products significantly. This would be expected from the proposed mechanism in Scheme 5, because the formation of the nitrile **6** and the oxime **7** would not be affected by the presence of nucleophiles.

On the other hand, a change in the anion of the nitrosyl salt plays a major role in the product distributions. Thus, nitrosyl chloride promotes the formation of phenylacetonitrile (**6**), α-hydroxylaminophenylacetoni-

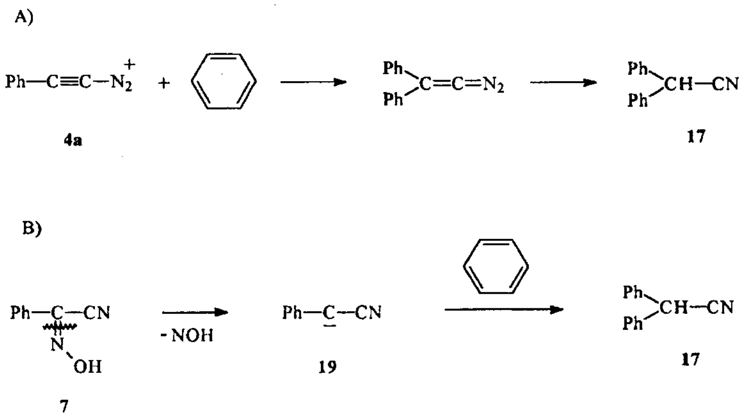
Table 1. Nitrosation reaction of the bis-silylated ynamine **3a** (main products, %)[a]

Reaction conditions	$PhCH_2CN$ (**6**)	 $PhC(=NOH)CN$ (**7**)	 $PhC(=O)CN$ (**8**)	$PhC{\equiv}CSiMe_3$ (**9**)	 (**10**)	$PhCN$ (**11**)
$NOBF_4$, CH_2Cl_2, Et_4NBr	6–52	10–63	2–15	5–14	1–5	3
$NOBF_4$, C_6H_6	22–82	5–45	0·3–5·3	1–3	0·3–2·2	2·5–3·2
$NOSbCl_6$, C_6H_6	1·4–10·9	11·7–18·4	1·5–5·2	1·4	1·1–1·3	1·8
$NOCl$, CH_2Cl_2	5–69	15·5–31	7·8	–	–	5·5
$NOTfO$, CH_2Cl_2	50–60	16·7–22.1	–	–	–	–

[a] The products were identified by GC–MS and by comparison of their properties with those of commercial samples or with samples prepared according to literature methods.



Scheme 5



Scheme 6

Me$_3$SiOSiMe$_3$	PhCH═CHCN	PhC—CN ‖ N OSiMe$_3$	PhCH$_2$COBr	PhC≡CPh	(Ph)$_2$CHCN	PhCHCN $\vert$ Cl
(12)	**(13)**	**(14)**	**(15)**	**(16)**	**(17)**	**(18)**
1	3–9	1·5	0·3	–	–	–
2–19·9	1–4	0·7	–	0·4	–	–
12·5–12·6	–	18·1–55	–	–	22·4	5·2–11·4
12·9	3·8	41.6	–	–	–	–
–	–	–	–	–	–	–

trile (**7**) and its silylated precursor **14**, whereas **14** is not detected in the reaction with nitrosyl triflate. The adventitious moisture present in the reaction could hydrolyse nitrosyl triflate with the formation of a trace amount of the strong triflic acid, which would catalyse the transformation of **14** into **7**.

An explanation for the formation of diphenylacetonitrile (**17**) is more speculative. Possible intermediates are a ethynyldiazonium ion **4a** [Scheme 6 (A)] or the carbene **19** formed in the homolytic cleavage of **7** [Scheme 6 (B)]. The nitrile (**17**) is formed only with nitrosyl hexachloroantimonate at the expense of **6** and **7**, in agreement with the proposed mechanism [Scheme 6 (B)].

On the other hand, α-chlorophenylacetonitrile (**18**) is detected only in the reaction of **3a** with nitrosyl hexachloroantimonate. The formation of **18** can be explained by the reaction of the carbene **19** with the nitrosyl salt in accordance with the proposed mechanism in Scheme 6 (B).

Benzoyl cyanide (**8**) was formed by hydrolysis of **7**. Trimethylsilylphenylacetylene (**9**) is a byproduct formed in the synthesis of the starting material **3a**. Dicyanostilbene (**10**) could be formed from **19** via a dimerization process (see Scheme 6).

We have no satisfactory explanation for the formation of benzonitrile (**11**) and 1-cyano-2-phenylethene (**13**).

CONCLUSION

The more nucleophilic centre in the bis-silylated ynanines is the β-carbon atom. This is supported by the products formed in the reaction with nitrosyl ion. This reaction does not lead to the expected attack at the nitrogen atom with the formation of ethynyldiazonium ion.

EXPERIMENTAL

The bis-silylated ynamines **3a** and **3b** were prepared according to reported methods.[10] Nitrosyl tetrafluoroborate (Merck) was used without purification. Nitrosyl chloride, nitrosyl hexachloroantimonate and nitrosyl triflate were prepared according to the literature.[11]

Nitrosation reaction; general procedure. To a suspension of the appropriate nitrosyl salt (1.2 mmol) in the corresponding anhydrous solvent (5 ml) (see Table 1) at −78 °C was added dropwise the silylated ynamine **3a** (1.2 mmol) in the same solvent (5 ml) under a nitrogen atmosphere. The mixture was stirred for 1 h and 1.2 mmol of Et_4NBr in the same solvent (4 ml) was added. When the reaction mixture had reached the room temperature, the reaction mixture was analysed directly by GC–MS (Table 1).

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