

A STUDY OF THE SILYLATION REACTION OF CYANOEPOXIDES WITH TRIMETHYLCHLOROSILANE IN THE PRESENCE OF MAGNESIUM

M. Bolourtchian, A. Saednya, R. Nouri

Chemistry and Chemical Engineering Research Center of Iran, P.O.Box 14335-186 Tehran, Iran

Laboratory of Organic Chemistry & Organosilicone Compounds, Faculty of Science, University of Tabriz, Tabriz, Iran

Abstract

In the presence of magnesium and hexamethylphosphorictriamide, HMPT, trimethylchlorosilane, TMS-Cl, reacts with cyanoepoxides to give related compounds. Ring cleavage at β -position of cyanoepoxide, **1**, followed by the addition of two trimethylsilyl groups leads to **2** then substitution of OSiMe₃ by trimethylsilyl or H takes place to give α, β -bis (trimethylsilyl) nitrile or β -trimethylsilylnitrile, respectively. Silylation reaction of cyanoepoxide **4** gives compounds **5** and **6**, but silylation of **9** gives only β -monosilylated derivative **10**. Silylation of α, β -diphenylcyanoepoxide, **11**, leads to polysilylated products, by participation of both nitrile and epoxide functions.

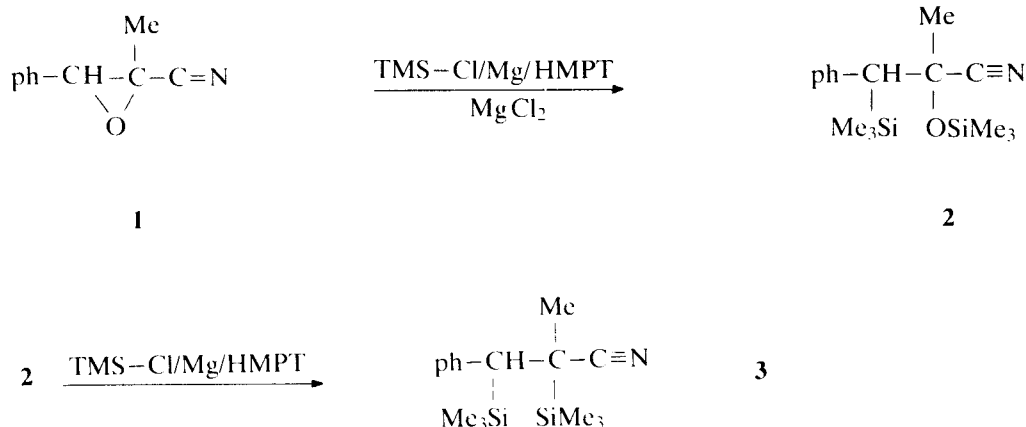
Introduction

It has been reported earlier [1,2,3] that trimethylchlorosilane, in the presence of magnesium and HMPT as solvent, reacts with conjugated nitrile to give α, β -disilylated nitriles. In the case of α, β -diphenylcinnamitrile polysilylated compounds are obtained. The similarity between the double bond and the epoxide ring led us to study the silylation reaction of epoxides, whose preparation is sim-

ple [4]. Therefore we have developed a simple method for the synthesis of α, β -disilylnitriles and β -monosilylnitrile, with good yields.

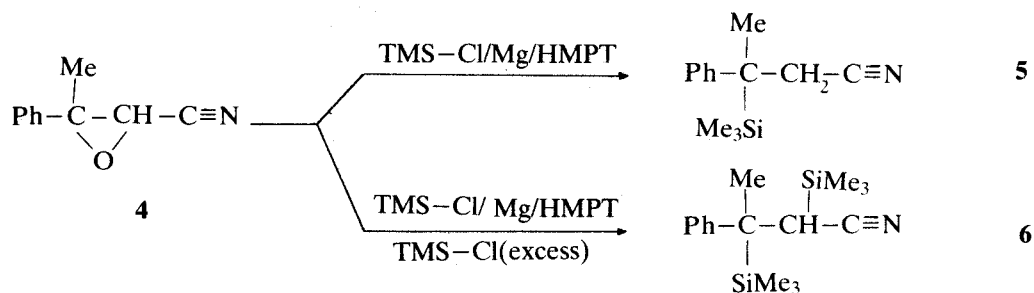
Results and Discussion

(a) According to the following reaction, silylation of **1** with Me₃SiCl/Mg/HMPT led to the formation of α, β -disilylnitrile **3**.

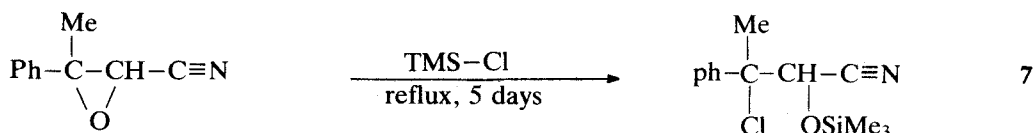


Key words: Silylation, Cyano-epoxides, Trimethylchlorosilane, Mg

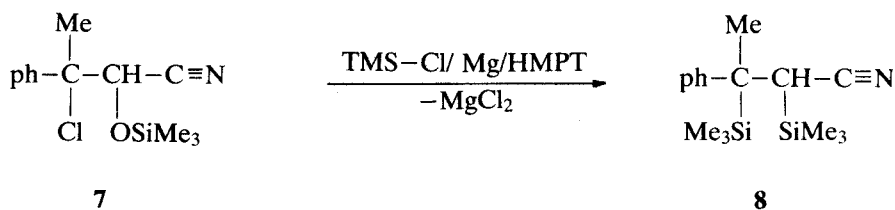
(b) Silylation of **4** with trimethylchlorosilane/Mg/HMPT produces β -trimethylsilylnitrile **5**. However, in the presence of excess TMS-Cl, disilylated derivative **6** can be obtained.



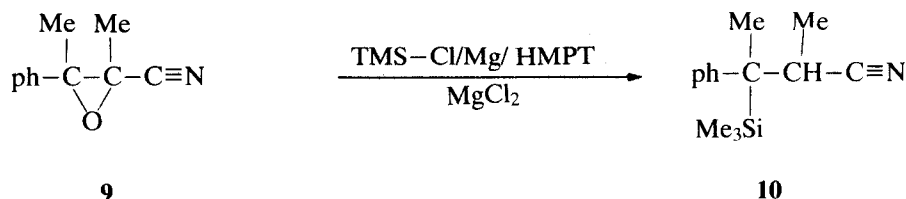
Direct reaction of trimethylchlorosilane with **4** at reflux temperature for five days, gives the adduct product **7**.



Further silylation of the adduct **7** with TMS-Cl/Mg/HMPT leads to the formation of α,β -disilylnitrile **8**.



(c) Silylation of **9** with TMS-Cl/Mg in HMPT produces only monosilylated derivative **10** but in the presence of excess TMS-Cl disilylated derivative was not obtained.

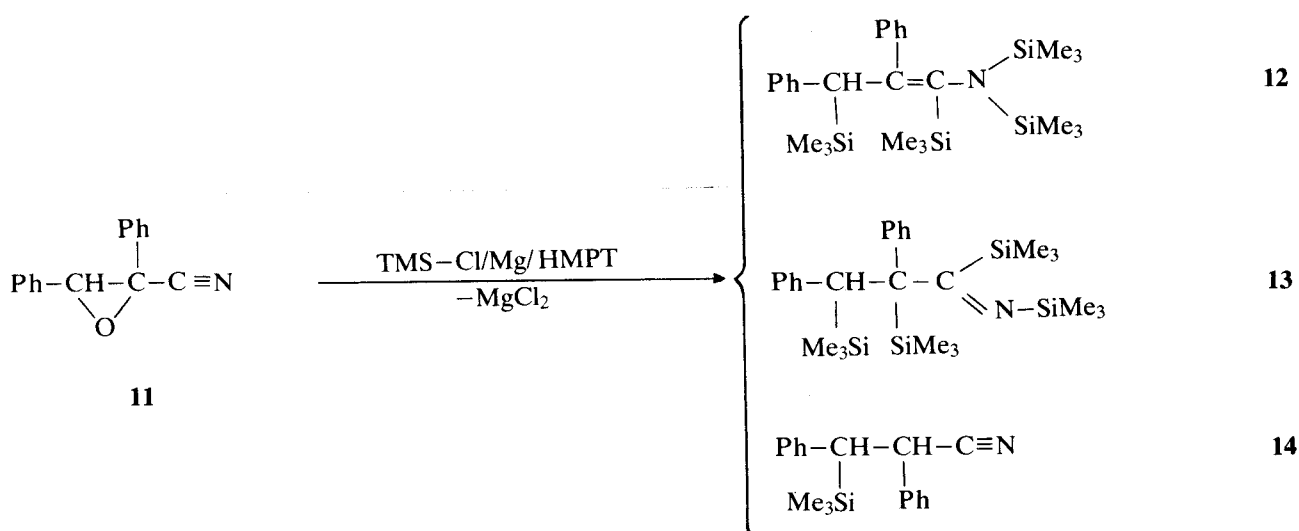


Structures of the products have been confirmed by NMR, IR, and Mass spectrometric studies. The results (yield, $\text{C}\equiv\text{N}$ frequency in IR, and m.p.) are

shown in Table 1.

(d) Silylation of **11** in the system of $\text{Me}_3\text{SiCl/Mg/HMPT}$, gives the compounds **12**, **13**, and **14**.

Products	Yield %	m.p. (C)	C≡N cm ⁻¹
3	50	106	2210
5	62	70	2220
8	60	65	2240
10	10-15	99-100	2240
12	16	251-2	-
13	36 57-62	225-230	-
14	5-10	-	2235



The mechanisms of the above reactions are shown in Scheme 1(5,6).

Experimental

The silylation conditions were similar to those reported earlier [1], [2]. The NMR spectrum data are given in the corresponding references.

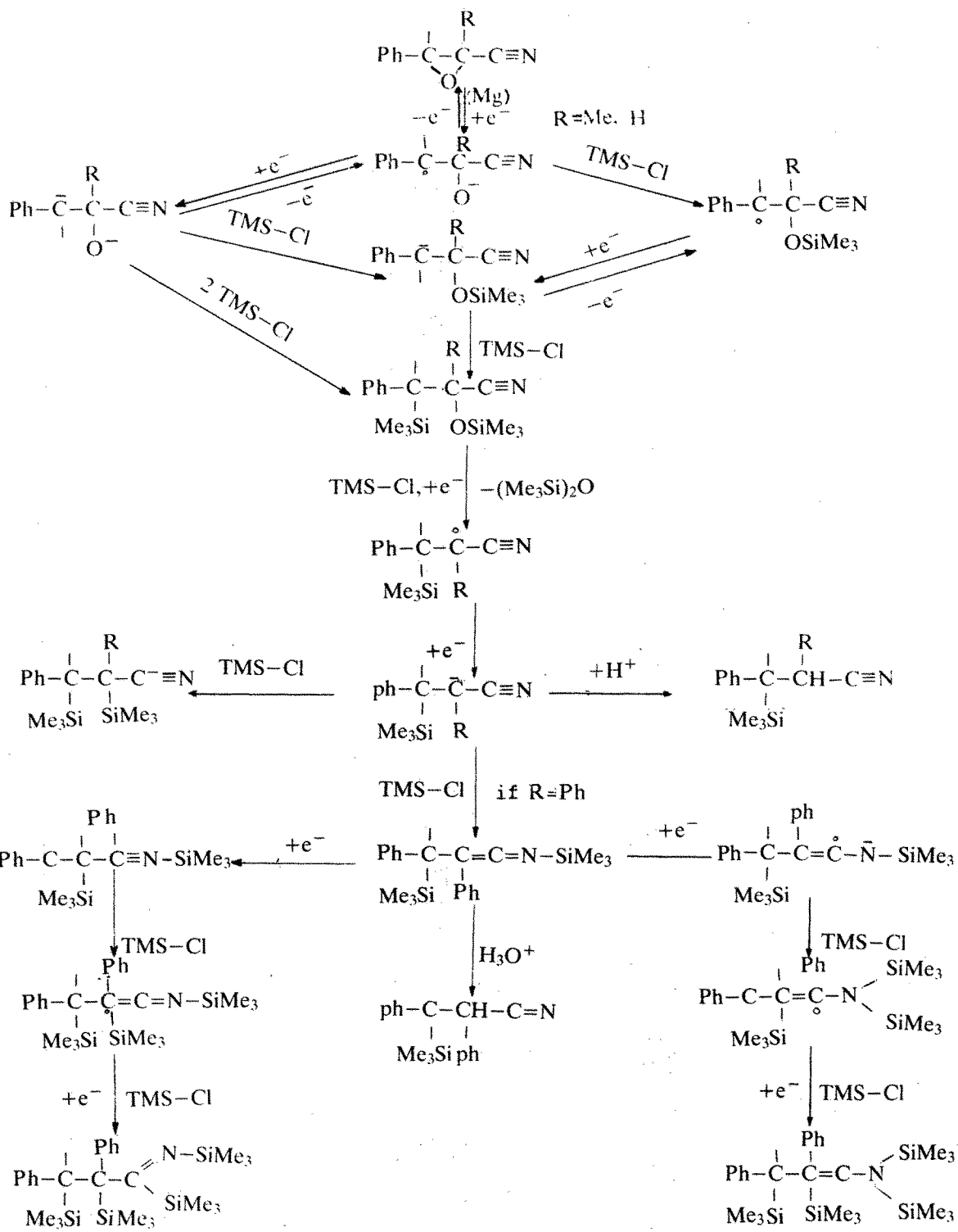
The NMR spectrum of **3** showed peaks at δ -0.16 (s, 9H), 0.08 & 0.1 (two singlets, 9H), 1.5 (s, 3H), 1.96 (s, 1H), and 6.84-7.82 (m, 5H). The NMR spectrum of compound **5** showed peaks at δ -0.05 (s, 9H), 1.56 (s, 3H), 2.8 (d of d, 2H, J=16 Hz), and 7.22-7.55 (m, 5H). The NMR spectrum of compound **8** showed peaks at δ -0.1 (s, 9H), 0.0 (s, 9H), 1.58 (s, 3H), 2.66 (s, 1H), and 7.04-7.30 (m, 5H). The NMR spectrum of compound **10** showed peaks at δ -0.02 (s, 9H), 1.32 (d, 3H, J=7 Hz), 1.43 (s, 3H), 3.22 (q, 1H, J=7 Hz), and 7.22-7.41 (m, 5H). The NMR spectrum of compound **12** showed peaks at

δ -0.23 (s, 9H), 0.0 (s, 9H), 0.02 (s, 9H), 0.41 (s, 9H), 4.56 (s, 1H), and 6.8-7.61 (m, 10H); compound **13** showed peaks at δ -0.19 (s, 9H), -0.09 (s, 9H), 0.0 (s, 9H), 0.36 (s, 9H), 3.68 (s, 1H), and 6.65-7.3 (m, 10H); compound **14** showed peaks at δ 0.06 (s, 9H), 2.47 (d, 1H, J=7 Hz), 4.22 (d, 1H, J=7 Hz), and 7.4-7.37 (m, 10H).

Conclusion

Silylation reactions of the cyanoepoxides lead to the following results:

- (1) Presentation of a new method for the formation of carbon-silicon bond by application of cyanoepoxides.
- (2) Synthesis of novel organosilicon compounds, the preparation of which is difficult by other methods.
- (3) Comparison of the reactivity of the easily obtained cyanoepoxides with corresponding α - β -unsaturated nitriles, which was reported earlier [1].



Scheme 1

Acknowledgements

We thank Dr.Mohammad R.Saidi for his assistance in interpretation and reporting the NMR spectrum data.

The abstract of this work was presented in the Eighth International Symposium on Organosilicon Chemistry, USA, 1987.

References

1. M.Bolourtchian, R. Calas, J. Dunogues, and N. Daffaut; *J. Organometal. Chem.*, **33**, 303(1971).
2. M.Bolourtchian and A. Saednya: *Bull. Soc. Chem. Fran.*, **11**, 170(1978).
3. M.Bolourtchian; Thesis d'Etat, Bordeaux (1972)
4. R.Rustoni; *Gazz. Chem. Ital.*, **69**, 378(1939).
5. R.Calas and J.Dunogues; *J.Organometal. Chem. Libr.*, **2**, 297 (1976).
6. R.Calas; *J.Organometal. Chem.*, **200**, 11(1980).