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BIS (TRIMETHYLSILYL) AMIDE AS NITRILE PRECURSOR

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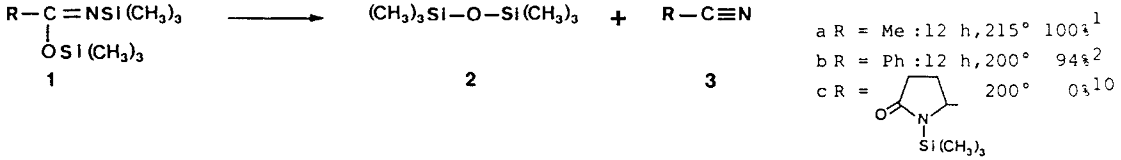
Abstract : Bis (trimethylsilyl) amides are converted into nitriles with high yields when they are treated wich a catalyst (tetrabutylammonium fluoride, Lewis acids or iron phthalocyanine).

Since its discovery, (1962)[1,2], the thermal decomposition of bis (trimethylsilyl) amides to nitriles has only be reported in two reviews[3,4],and has never been used as a preparative method for nitriles synthesis;recent reviews on silicon chemistry do not report this reaction[5-8].



However this thermal reaction is not general and, for instance, compound 1c remains inaltered under these conditions. In this paper we describe the catalytic decomposition of silylated amides :

Catalyst

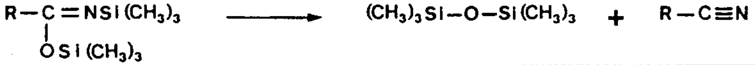
Three different catalysts promote the decomposition of 1b used as a model compound :

- Tetrabutylammonium fluoride, which is a very soluble form of fluoride ion, can be used in this reaction (20 h ; 15° ; 100%). Less soluble fluoride compounds do not promote the decomposition to nitrile at room temperature.
- True Lewis acids such as $FeCl_3$ (1 h, 15°, 100% ; 40 h, -70°, 50%), $ZnCl_2$ (10mn, 65°,100%) or $AlCl_3$ (2 h, 20°, 95%) are very efficients catalysts.
- Iron phthalocyanine, also catalyses this decomposition at 75° (6 h, 100%). This compound is of special interest because it is the first time that it has been used in siloxane elimination ; cobalt and fluorochromium phthalocyanines are unreactive at 90°.

Scope of the reaction (table I)

As evidenced in the table, this siloxane elimination is general and succeeds in every case , except when R is a strong withdrawing group . Another important feature is that the catalysts are complementary because they do have not the same sensitivity to the structure of the molecule : when iron trichloride is partly deactivated by a basic group, fluoride ions are not deactivated, and when fluoride cannot be used at room temperature, iron trichloride can be utilized.

TABLE I. NITRILE SYNTHESIS BY ELIMINATION OF HEXAMETHYLDISILOXANE



$$R-\underset{OSi(CH_3)_3}{\underset{|}{C}}=NSi(CH_3)_3 \longrightarrow (CH_3)_3Si-O-Si(CH_3)_3 + R-C\equiv N$$

N°	R	Catalyst : $nBu_4N^+F^-$, $3H_2O$[a]			Catalyst : $FeCl_3$[a]		
		t(hour)	T°C	Yield %[b]	T(hour)	T°C	Yield %[b]
1	C_6H_5-	20	15	100	1	15	100
2	2-$Me_3SiOC_6H_4$-	20	90	100[c,d]	0.5	18	100
3	3-Py-	22	20	95	0.5	80	100[d]
4	nC_3H_7-	17	19	95	1	19	95
5	CH_3-[e]	3	20	75	0.5	20	100
6	Pyro-[f]	3	80	100	5	80	95
7	CF3-[h]	20	55	0	20	55	0

[a] Disilylamide : 1g ; catalyst : 0.02g. [b] NMR yield. [c] 83.3% of isolated yield of 2-cyanophenol, after distillation, methanol solvolyse and acticarbon treatment. [d] No reaction at 20°. [e] Aldrich. A minute amount (2%) of acetonitrile found in this commercial product is probably the result of this easy hexamethyldisiloxane elimination. [f] Compound 1c.

This two-steps procedure for the dehydration of amides can be effected in one-step without isolation of the bis (trimethylsilyl) amide : for instance heating nicotinamide(6 g) with trimethylchlorosilane (7 ml), triethylamine (30 ml) and zinc chloride (0.6 g) give a triethylamine solution of bis (trimethylsilyl) derivative 1 (R=3-Py) ; when the solvent was evaporated and the residue distilled in-vacuo, nitrile 2 was obtained in 79% yield ; in the same way, compound 3c was obtained in 91% yield in a preparative scale[10]. Thus this method can be used as an alternative to other one-step procedures for the preparation of nitriles[11,12].

This work significantly extends the scope of nitrile synthesis using silyl amides : only a catalytic amount of an acidic ($FeCl_3$), basic (F^-) or neutral (PcFe) compound is necessary to promote this reaction, in contrast to the published decomposition reaction of a monosilylamide by an equimolar amount of an acidic reagent (acid chloride[13] or thionyl chloride[14]).

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