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CYCLIZATION REACTIONS BY THE USE OF 1,2-BIS(TRIMETHYLSILYL)IMINO-1,2-DIPHENYLETHANE

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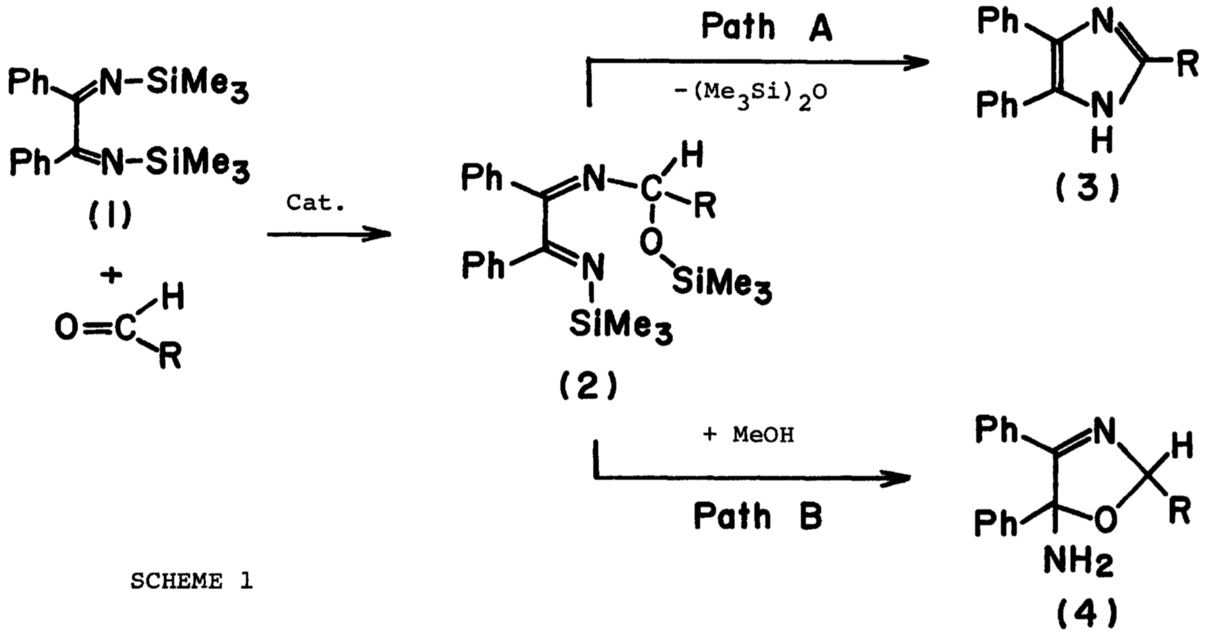
Imidazole (3) or oxazoline (4) derivatives are obtained by the reactions of 1,2-bis(trimethylsilyl)imino-1,2-diphenylethane with carbonyl compounds after thermolysis or methanolysis of the common intermediate (2) of which thermal stability seems to depend on the electronic character of R.

A dual character of N-(trimethylsilyl)diphenylmethylenamine was previously reported in a unique synthesis of nitrogen containing heterocycles,[1, 2, 3] in which an insertion of polar unsaturated compounds into a silicon nitrogen bond and subsequent participation of the imino group played an important role as key steps. 1,2-Bis(trimethylsilyl)imino-1,2-diphenylethane (1) is an interesting model from the view point of the formation of heterocycles because it possesses two N-trimethylsilylimino groups in a same molecule. We now report the formation of imidazole and oxazoline derivatives as the result of different types of cyclization via the reaction of (1) with aldehydes.

1,2-Bis(trimethylsilyl)imino-1,2-diphenylethane (1), readily available from benzil via N-lithio-bis(trimethylsilyl)amide route,[4] gave 2,4,5-triphenylimidazole (3a) in 83% yield with the liberation of hexamethyldisiloxane when the mixture of (1), an equivalent of benzaldehyde, and catalytic amount of aluminum chloride was heated in benzene for 12 hr at about 90°C. Although the present reaction resembles the intermolecular deoxygenation reaction of N,N'-bis(trimethylsilyl)ethylenediamine derivatives with aldehydes,[5] Lewis acid catalyst is indispensable in this case, which may imply low nucleophilicity of (1) compared with ethylenediamine derivatives. Imidazoles (3b ∿ g) were also obtained from a similar reaction with aldehydes containing relatively electron donating groups. The virtual difference of the effect as catalyst was not observed between aluminum chloride and ammonium sulfate.

On the other hand when p-nitrobenzaldehyde was heated under reflux with equimolar amount of (1) and catalytic amount of ammonium sulfate for 19 hr in benzene, the (1:1) insertion product (2) was obtained. It was supported by the disappearance of $\nu_{C=O}$ band and the appearance of two separated trimethylsilyl signals (δ: 0.15 and 0.25) in the i.r. and n.m.r. spectrum, respectively. Treatment of the (1:1) reaction mixture with an excess of methanol gave strikingly 5-amino-2-p-nitrophenyl-4,5-diphenyl-3-oxazoline (4a) in 82% yield as desilylated product. Oxazoline (4b ∿ e) were formed by analogous reactions with m-nitrobenzaldehyde, p-cyanobenzaldehyde, chloral and bromal, respectively. The results are summarized in scheme 1 and the table.

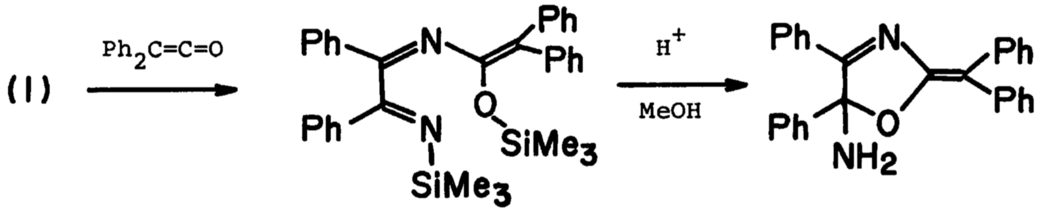
The formation of imidazole (3) and oxazoline (4) are interpreted by assuming the intervention of insertion products (2) as shown in scheme 1. An intra-



SCHEME 1

Table Reactions of (1) with aldehydes

Aldehydes	Catalyst	Reaction time (hr)	Products (path)	Yield (%)	M.P.s (°C)
C_6H_5CHO	$AlCl_3$	12	3a (A)	83	278 - 279
p-MeO-C_6H_4CHO	$AlCl_3$	12	3b (A)	98	231 - 232
p-Me-C_6H_4CHO	$AlCl_3$	12	3c (A)	95	180 - 182
p-Cl-C_6H_4CHO	$AlCl_3$	12	3d (A)	72	264 - 265
m-Cl-C_6H_4CHO	$AlCl_3$	12	3e (A)	56	308 - 310
p-NO_2-C_6H_4CHO	$(NH_4)_2SO_4$	65	3f (A)	95	237 - 238
Me_2N-CHO	$(NH_4)_2SO_4$	48	3g (A)	99	245 - 248
PhCH=CH-CHO	$(NH_4)_2SO_4$	39	3h (A)	57	224 - 226
p-NO_2-C_6H_4CHO	$(NH_4)_2SO_4$	19	4a (B)	82	163 - 164
p-CN-C_6H_4CHO	$(NH_4)_2SO_4$	26	4b (B)	62	157 - 158
m-NO_2-C_6H_4CHO	$(NH_4)_2SO_4$	26	4c (B)	59	105 - 107
Cl_3C-CHO	$(NH_4)_2SO_4$	13	4d (B)	81	126 - 130
Br_3C-CHO	$(NH_4)_2SO_4$	14	4e (B)	58	188 - 189
Ph_2C=C=O	--	1	6 (B)	71	185 - 186



(5) (6)

molecular elimination of hexamethyldisiloxane from (2) would lead to the formation of imidazole (3) (path A) while a nucleophilic attack of oxygen atom toward another trimethylsilyl imino carbon atom would result in cyclizing to oxazolines (4) during the treatment of (2) with an excess of methanol (path B). The intermediacy of (2) was confirmed by the selective formation of (3f) from the (1:1) reaction mixture on heating for prolonged period (65 hr). Further direct evidence is the isolation of (1:1) insertion product (5) in the reaction of (1) with diphenylketene, which was cyclized to oxazoline (6) by protodesilylation in acidic methanol. The easiness of the ω-elimination of hexamethyldisiloxane seems to depend on the electronic character of aldehydes. An electron withdrowing group R in aldehydes would prevent the elimination of siloxy group from (2) and give enough stability to survive under the reaction condition. The border exists between chloro and cyano substituents in p-substituted benzaldehydes.

The latter cyclization is much interesting because (1) behaves formally as a 3 component of [3+2] cycloadditions. Same oxazoline skeltons can be obtained only through 1,3-dipolar cycloaddition of nitrile ylide 6) or photo reaction of aziline with carbonyl compounds. 7, 8)

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9. Satisfactory elemental analyses and spectra were obtained for 3 - 6.

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