

## REACTIVITY OF ACYLSILANE PHENYLHYDRAZONES WITH PHOSPHORUS TRICHLORIDE

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**Abstract:** Nitriles are obtained from reaction of acyltrimethylsilane phenylhydrazones with phosphorus trichloride, whereas under the same experimental conditions triphenylsilyl derivatives decompose and *t*-butyldimethylsilyl derivatives do not react. Evidences of the reaction pathway are reported.

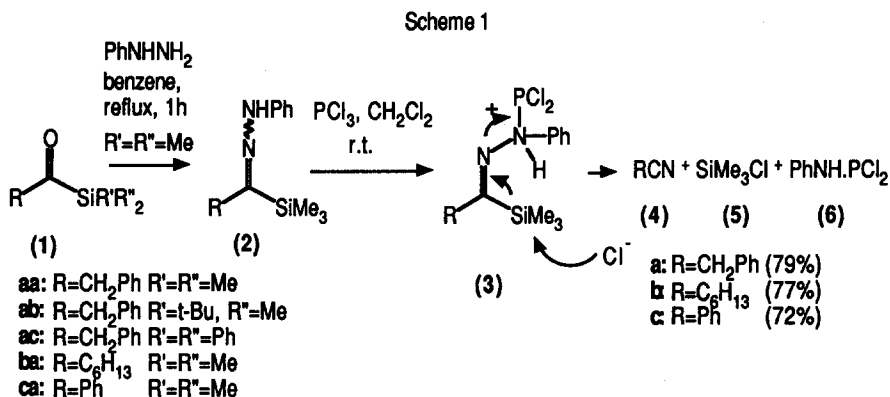
Chemical literature offers poor examples of condensation reactions of the carbonyl group in acylsilanes.<sup>1</sup> Perhaps the most worthy of note is the synthesis of silyldiazoalkanes via tosylhydrazones.<sup>2</sup>

Recently, the reaction of ketone phenylhydrazones and phosphorus trichloride was found to be a facile and versatile method for the synthesis of functionalized indoles.<sup>3</sup> The extension of this reaction to acylsilane phenylhydrazones seemed a promising route to 2-trialkylsilylindoles, since very few methods of synthesis of these derivatives are reported.<sup>4</sup> However, allowing the phenylhydrazone of (phenylacetyl)trimethylsilane to react with phosphorus trichloride in dichloromethane at room temperature, aniline and phenylacetone nitrile were unexpectedly recovered in 79% yield.<sup>5</sup> Nitriles can be obtained both from aromatic and aliphatic trimethylsilyl ketones, whereas triphenyl derivatives underwent decomposition<sup>2</sup> and *t*-butyldimethyl ones are unaffected under these experimental conditions. Indole formation was never observed. Both phosphorus oxychloride and thionyl chloride are able to give nitriles in comparable yields but in longer reaction times (overnight vs. one hour). On the other hand, no reaction was observed bubbling hydrogen chloride into the solution of the hydrazone.

<sup>1</sup>H and <sup>31</sup>P NMR spectroscopic data suggest a pathway where a coordination of the phosphorus atom on aminic nitrogen occurs. A subsequent nucleophilic attack of chloride ion on silicon atom causes desilylative  $\beta$ -elimination<sup>7</sup> from intermediate **3** to nitrile **4** and aminophosphine **6** (scheme 1). In fact, immediately after the mixing of reactants, <sup>31</sup>P-NMR showed a signal at  $\delta=105^{\delta}$  (very likely the complex **3**) which disappeared at completion of the reaction when the signal of complex **6**<sup>9</sup> was exclusively detected. <sup>1</sup>H-NMR signals of the trimethylsilyl frameworks of **3** shifted to the trimethylchlorosilane one as well as signals of the methylene groups shifted to the chemical shift of the methylene of phenylacetone nitrile. Moreover GC-MS analysis of the mixture from the reaction of (phenylacetyl)trimethylsilane with thionyl chloride revealed the formation of comparable amounts of phenylacetone nitrile and sulfenyl aniline.

In conclusion a new mild route to nitriles, based on a peculiar reactivity of acyltrimethylsilane phenylhydrazones so far unknown, is available. Nevertheless, since acylsilanes can be obtained only with multi-steps procedures,<sup>8</sup> this way cannot compete with other simple reactions.<sup>10</sup> Furthermore, it offers another example of the important role played by

phosphorus trichloride in promoting reactions of hydrazones.<sup>3,11</sup> Studies are in progress to extend this reaction to the formation of double or triple carbon-carbon bonds<sup>7a</sup> starting from  $\alpha$ -silylated nitrogen derivatives.



**Acknowledgements** We thank Prof. G. Baccolini for helpful discussion and Italian M.U.R.S.T. for financial support.

#### References and Notes

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5. In a typical procedure acylsilanes<sup>6</sup> were dissolved in benzene and a stoichiometric amount of phenylhydrazine was added. The mixture was refluxed for about one hour in a Dean-Stark apparatus to remove water. Benzene was then evaporated under reduced pressure and the residue was dissolved in dichloromethane before adding equimolecular amounts of phosphorus trichloride. The reaction was monitored by TLC analysis, then quenched, extracted with dichloromethane, evaporated, and filtered on a short silica gel column (eluant hexane:diethyl ether 4/1). Aniline was recovered from neutralized aqueous layer by extraction with diethyl ether. Products were obtained in 70-80% yield calculated on starting acylsilane and recognized by comparison with authentic samples.
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8. Downfield shift from 85% aqueous phosphoric acid as external standard. Recorded on a Varian FT80 instrument.
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(Received in UK 24 September 1990)