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AN IMPROVED SYNTHESIS FOR N,N'-THIOCARBONYL-DIIMIDAZOLE

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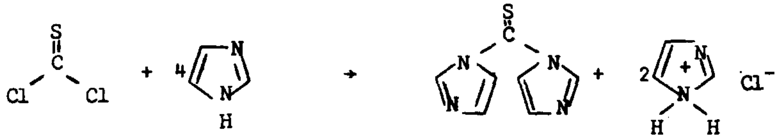
The recent report of an elegant stereospecific olefin synthesis by Corey and Winter (1) and its very practical application in the synthesis of unsaturated sugars by Horton and Turner (2) have aroused great interest. An important intermediate in this synthesis is N,N'-thiocarbonyldiimidazole, I.

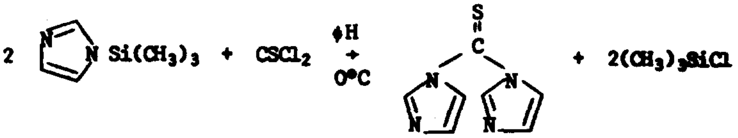
Compound I first was reported by H. A. Staab (3), who prepared it according to the equation 1. In his report he gave no experimental details.

1. 

Staab observed a melting point of 103-105°C for I. Later Ried and Beck (4) reported the preparation of I by the same reaction using benzene as solvent. They observed a melting point of 95°C for the material obtained after recrystallisation from pet. ether. H. A. Staab and G. Walther (5) in a later more detailed paper disputed the properties of I given by Ried and Beck. The preparation of I they described as according to equation 1 using a mixture of benzene and chloroform as solvent. The imidazolinium hydrochloride which precipitated during the course of the reaction was filtered off and the filtrate on evaporation gave a compound melting at 96-100°C. Recrystallisation from tetrahydrofuran followed by sublimation in vacuo gave yellow crystals of I having a melting point of 105-106°C.

The most recently described method of Staab and Walther is time consuming and much effort is necessary to obtain a pure product. We have prepared I according to equation 2.

2.



Trimethylsilylimidazole was prepared according to the method of Birkoffer and Ritter (6) and the thiophosgene by the reduction of perchloromethylmercaptan using tetralin (7). The volatile trimethylchlorosilane and the solvent can be removed by vacuum distillation at room temperature. The bright yellow residue obtained directly from this reaction, without tedious crystallisation and sublimation, is analytically pure and has the same melting point and infrared spectrum as that for the purified compound reported by Staab and Walther. The yield is essentially quantitative.

In a typical preparation, 18.2gm (130 mmoles) of trimethylsilylimidazole was placed along with 100cc of anhydrous benzene (distilled from CaH_2) in a dry 200ml round bottom flask fitted with a reflux condenser carrying a drierite tube. The flask had a side arm closed off with a serum cap. The contents were cooled with an ice bath. The solution was stirred magnetically and 7.5gm (65 mmoles) of thiophosgene was slowly introduced from a syringe into the reaction flask through the serum capped side arm. Reaction ensued immediately. After the addition was complete the contents were stirred for another hour to ensure the total reaction. The condenser was replaced with a vacuum take-off with a stream of dry nitrogen sweeping the apparatus. The reaction vessel then was evacuated and all the volatiles (benzene and trimethylchlorosilane as demonstrated by gas-chromatography) were pumped off into a liquid nitrogen cooled vapor trap. The bright yellow powder remaining in the reaction vessel at the end of this distillation can be used directly without additional purification for further experiments.

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1) E. J. Corey and R. A. E. Winter, J. Am. Chem. Soc., 85, 2677 (1963)

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3) H. A. Staab, Angew. Chem., 73, 148 (1961)

4) W. Ried and B. M. Beck, Ann., 646, 96 (1961)

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6) L. Birkoffer and A. Ritter, Angew. Chem. Internat. Edit., 4, 427 (1965)

7) M. Bögemann, S. Peterson, O. E. Schultz and H. Söll, in Hounben, Weyl-Muller, "Methoden der organischen chemie", part 4, Vol. 9, Page 789, Verlag G. Thieme, Stuttgart (1955)