Journal of Organometallic Chemistry, 99 (1975) C5–C7

Preliminary communication

REACTION OF TRIMETHYLSILYL CYANIDE WITH CARBODIIMIDES

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(Received June 18th, 1975)

Summary

Trimethylsilyl cyanide react with carbodiimides in the presence of aluminum trichloride to give 1/1 adducts, *N*-trimethylsilyl-1-cyanoformamidines (I), in high yields. At rather high temperatures (150-200 °C) the reaction also proceeded without catalyst. The 1/1 adduct reacted with isocyanates and carbodiimides forming 4,5-diiminodiazolidine-2-one and 2,4,5-triiminoimidazolidine, respectively.

Recently, it has been shown that trimethylsilyl cyanide is a good reagent in organic syntheses for introducing a cyano group, and for protecting and activating carbonyl groups [1-3]. However, the reaction of trimethylsilyl cyanide with heterocumulenes has received only limited attention.

In the present communication, we describe the cyanosilylation of carbodiimides and its application to the synthesis of five-membered heterocyclic systems*

We found that trimethylsilyl cyanide reacts with *N,N'*-disubstituted carbodiimides in the presence of a catalytic amount of aluminum trichloride at ambient temperature to give *N,N'*-disubstituted *N*-trimethylsilyl-1-cyanoformamidines (I) in high yields. These adducts were easily solvolyzed to the corresponding 1-cyanoformamidines (II) by methanol or H_2O/ether in quantitative yield. Compounds I also were converted to *N*-acetyl-1-cyanoformamidines (III) by the action of acetyl chloride in nearly quantitative yield (Scheme 1).

In a typical procedure, 65 mg of aluminum trichloride (5 mol%) was added to a mixture of *N,N'*-diisopropylcarbodiimide (1.26 g, 10 mmol) and a slight excess of trimethylsilyl cyanide (1.19 g, 12 mmol) under nitrogen, and the mixture was stirred at ambient temperature for 4 h. After the reaction was completed, the reaction mixture was distilled under reduced pressure to give

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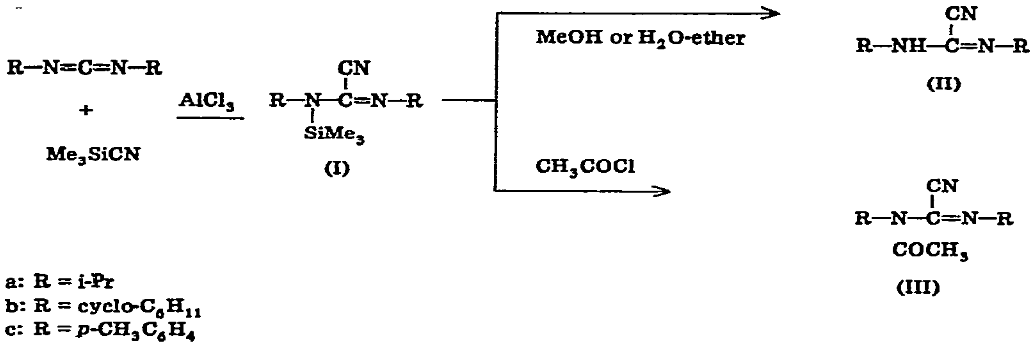
*IR, NMR and mass spectra and elemental analyses of all new compounds were consistent with the assigned structures.



SCHEME 1

1.89 g (84%) of *N,N'*-diisopropyl-*N*-trimethylsilyl-1-cyanoformamidine (Ia; b.p. 53°/1.3 mmHg). The yield of Ia estimated by direct hydrolysis of the reaction mixture was found to be 95%. In a similar manner, *N,N'*-dicyclohexyl- and *N,N'*-di-*p*-tolyl-*N*-trimethylsilyl-1-cyanoformamidines (Ib and Ic) were produced in nearly quantitative yields[*] (after hydrolysis 98 % and 96%, respectively).

Trimethylsilyl cyanide also reacted with *N,N'*-diisopropylcarbodiimide in the absence of the catalyst under more drastic conditions, e.g., 24 h at 190 °C, to give Ia in 85% yield. Similarly, the reaction of *N,N'*-dicyclohexylcarbodiimide with trimethylsilyl cyanide under the conditions described above, followed by hydrolysis afforded the 1/1 adduct IIb in 54% yield.

Cycloadditions of *N*-trimethylsilyl-1-cyanoformamidines (I) with isocyanates or carbodiimides were studied in connection with the reaction of isocyanates with trimethylsilyl cyanide, which gave cyclic 1/2 adducts (5-trimethylsilyliminodiazolidine-2,4-diones) [4]. The reaction of Ia with *p*-toluenesulfonyl isocyanate proceeded exothermally to afford 1-*p*-toluenesulfonyl-3-isopropyl-2-isopropylimino-5-trimethylsilyliminoimidazolidine-2-one (IVa), in quantitative yield, while the reaction of phenyl isocyanate with Ia required heating at 80 °C for 14 h to produce the cycloadduct, IVb, in 87% yield. In the presence of aluminum trichloride (5 mol%), however, the latter cycloaddition took place smoothly at ambient temperature to give IVb in excellent yield. The 5-trimethylsilyliminoimidazolidine-2-ones (IVa and IVb) thus obtained were easily converted to the corresponding 5-iminoimidazolidine-2-ones (Va or Vb) in quantitative yields by action of methanol.

In the case of carbodiimides, cycloaddition required drastic conditions. For example, the reaction of Ib with *N,N'*-dicyclohexylcarbodiimide proceeded at 190 °C (60 h), to afford a cycloadduct, 1,3-dicyclohexyl-4-cyclohexylimino-5-trimethylsilyliminoimidazolidine (IVc), in 56% yield. This product was easily converted to the corresponding 5-iminoimidazolidine (Vc) by methanol in

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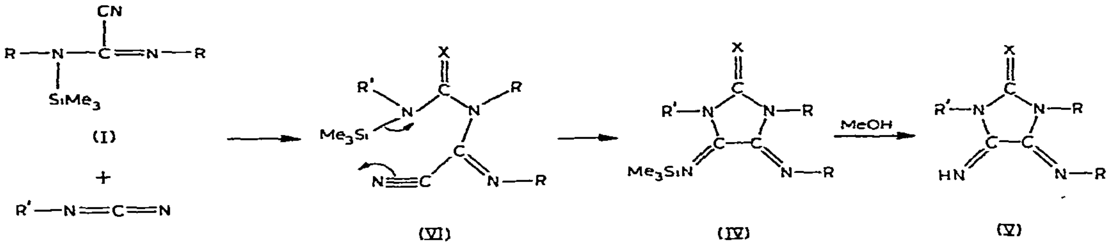
[*] Direct distillation of the reaction mixture of Ib resulted in partial decomposition (b.p. 118°/0.3 mmHg). However, a sample which was pure enough for elemental analyses was obtained when n-hexane was added to the reaction mixture and the precipitate, $AlCl_3$, was filtered off with a G-4 glass filter under argon at −10 °C and the filtrate was concentrated in vacuo. A pure sample of Ic which give satisfactory elemental analyses was obtained by recrystallization from n-hexane using a G-4 glass filter under argon at −78 °C.



a· $R = i\text{-}Pr$, $R' = p\text{-}CH_3C_6H_4SO_2$, $X = O$

b $R = i\text{-}Pr$ $R' = Ph$, $X = O$

c· $R = R' = cyclo\text{-}C_6H_{11}$, $X = cyclo\text{-}C_6H_{11}N$

quantitative yield. Addition of a catalytic amount of aluminum trichloride to the reaction system did not display a significant affect in contrast with the similar reaction of phenyl isocyanate.

As shown in Scheme 2, cycloaddition most likely is a stepwise process.

Further investigations and applications of the synthesis of heterocycles are now in progress.

References

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