Reaction of Trimethylsilyl Cyanide with Isocyanates

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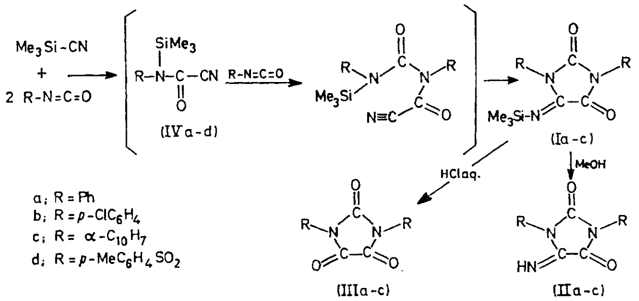
Summary Trimethylsilyl cyanide reacts with aryl isocyanates to give 5-iminodiazolidinediones (1 : 2 adducts), while tosyl isocyanate afforded the 1 : 1 adduct.

Recently, it has been shown that trimethylsilyl cyanide (TMSCN) is a good reagent for the preparation of cyanohydrin derivatives which can be used as selective carbonyl protective groups in organic syntheses.[1,2] Thermal and Lewis acid catalysed reactions of TMSCN with acyl halides or epoxides have also been reported.[2] We report here the addition of TMSCN to aryl isocyanates and tosyl isocyanate.

Table.

Compound	Mp. (°C)	Yield (%)
(Ia)	118—120	91
(Ib)	192—193	94
(Ic)	175—177	82
(IIa)[3]	137—138	98
(IIb)[a]	234—235	98
(IIc)	210—212	98
(IVd)	—	95

[a] See ref. 4, but analytical data are unclear.



TMSCN reacts (50 °C; 6 h) with 2 mol equiv. of aryl isocyanates with no catalyst to give the *NN′*-disubstituted 5-

trimethylsilyliminodiazolidinediones (I) in excellent yields, which could easily be converted into the corresponding 5-imino-compounds (II) with methanol, and hydrolysed to the diazolidinetriones (III) with hydrochloric acid.

p-Chlorophenyl isocyanate, phenyl isocyanate, and α-naphthyl isocyanate all gave the corresponding compounds (I), but tosyl isocyanate afforded only the 1:1 adduct (IVd) even with an excess of isocyanate. This may be due to the electron deficiency on the nitrogen atom of the silylamine unit of (IVd), which prevents electrophilic attack of a further tosyl isocyanate molecule.

The results are in the Table. The n.m.r. and i.r. spectra, and elemental analyses of all new compounds were consistent with the assigned structures.

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[1] D. A. Evans and L. K. Truesdale, *Tetrahedron Letters.*, 1973, 4929; D. A. Evans, L. K. Truesdale, and G. L. Carroll, *J.C.S. Chem. Comm.*, 1973, 55; D. A. Evans, J. M. Hoffman, and L. K. Truesdale, *J. Amer. Chem. Soc.*, 1973, **95**, 5822.

[2] W. Lidy and W. Sundermeyer, *Chem. Ber.*, 1973, **106**, 587; *Tetrahderon Letters*, 1973, 1449.

[3] W. Diekmann and H. Kämmerer, *Chem. Ber.*, 1905, **38**, 2977.

[4] H. Q. Smith and H. J. Miller, U. S. P., 1967, 3,484,525.