

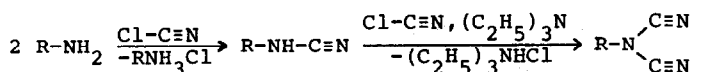
ADDITION OF NUCLEOPHILES TO ALKYL DICYANAMIDES¹

P.H. Benders

Laboratory for Organic Chemistry, Twente University of Technology,
Enschede, The Netherlands

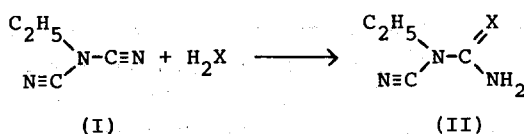
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Alkyldicyanamides have been synthesized recently², according to

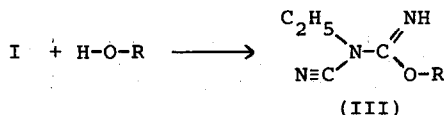


This paper reports on the addition of various nucleophiles to ethyl- and cyclohexyldicyanamide. In principle both cyano groups are accessible for nucleophilic attack. In practice, under the reaction conditions chosen, but one of the cyano groups is attacked.

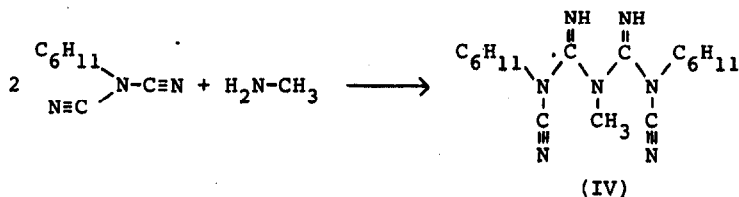
Treatment of ethyldicyanamide (I) with 20% sulfuric acid at 50°C for 20 h yields 1-cyano-1-ethylurea (II, X=O). The corresponding thiourea (II, X=S) is obtained by passing hydrogen sulfide through an ethereal solution of I, at room temperature, for 6 h.



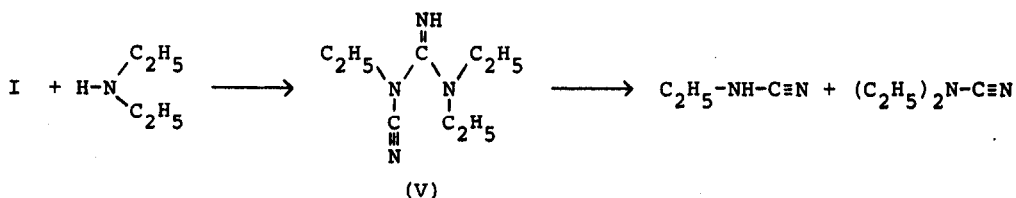
Both methanol³, and phenol in ethereal solution add to I at room temperature to give 1-cyano-1-ethyl-2-methyl- (III, R=CH₃) and 1-cyano-1-ethyl-2-phenylisourea (III, R=C₆H₅) respectively. The latter⁴ and related⁵ compounds were previously described as obtained from the addition of monocyanamides to aryl cyanates.



Equivalent amounts of methylamine and cyclohexyldicyanamide react to give 1,5-dicyano-1,5-dicyclohexyl-3-methylbiguanide (IV).



Diethylamine adds to I (etheréal solution, room temperature) to yield 1-cyano-1,3,3-triethylguanidine (V). On standing at room temperature V decomposes into a mixture of ethylmono- and diethylcyanamide.



So, various nucleophiles add to alkyldicyanamides under mild conditions. Apparently, dicyanamides, like cyanogen halides, sulfonyl cyanides and cyanic acid esters possess one activated cyano group⁶. Activation in this case may be ascribed to the electron - withdrawing effect of the second cyano group.

Compounds prepared:

- II , X=O , yield 73%, m.p. 125-6°C, from ethanol or chloroform
- II , X=S , yield 99%, m.p. 107°C, from benzene/carbon tetrachloride 1:1
- III, R=CH₃ , yield 74%, m.p. 34-5°C, b.p. 65-65.5°C/1.3 mm
- III, R=C₆H₅ , yield 84%, m.p. 35-6°C, b.p. 105°C/0.4 mm
- IV , yield 24%, m.p. 215-7°C decomp., from ethyl acetate
- V , yield 72%, b.p. 66-7°C/0.25 mm, n_D²⁰=1.4767

IR and NMR data, and elemental analyses agree with the proposed structures.

Notes and References

- 1) Chemistry of alkyldicyanamides II.Ref.2 is considered to be Part I in this series.
- 2) P.H.Benders and J.Th.Hackmann,Recueil Trav.chim.Pays-Bas 91,343(1972).
- 3) With ethanol refluxing is necessary.
- 4) D.Martin,K.Witke,P.Reich and K.Nadolski,Chem.Ber.101,3196(1968).
- 5) E.Grigat and R.Pütter,Chem.Ber.98,2619(1965).
- 6) A.M.van Leusen and J.C.Jagt,Tetrahedron Letters 1970,967 and literature cited there.