

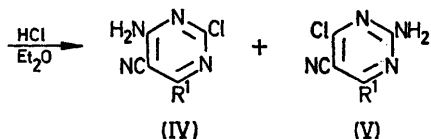
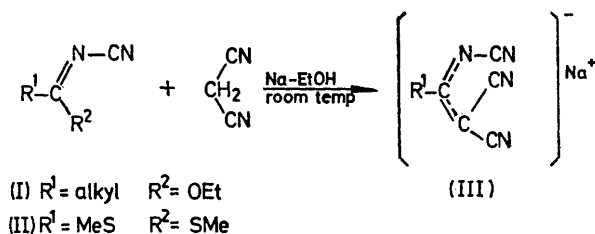
Synthesis of 5-Cyanopyrimidines

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Summary New syntheses of 5-cyanopyrimidines by the reaction of *N*-cyanoimides and dimethyl cyanoimidodithiocarbonate with malononitrile or ethyl cyanoacetate, respectively, are described.

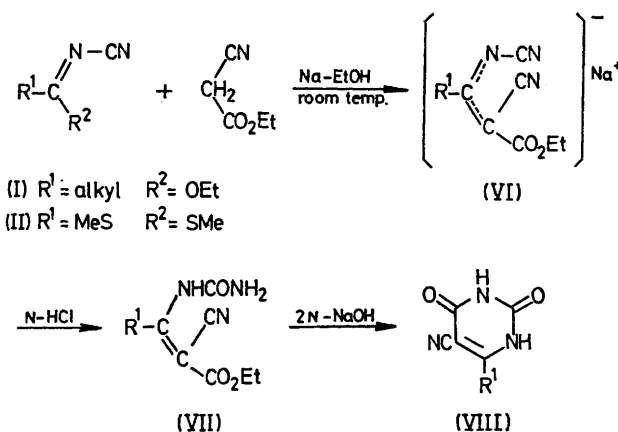
THE *N*-cyanoimides (I)¹ and dimethyl cyanoimidodithiocarbonate (II)² are readily available. We now report a new synthesis, with excellent overall yields, of 5-cyanopyrimidines by the reaction of (I) and (II) with malononitrile in EtOH (Scheme 1) or ethyl cyanoacetate (Scheme 2), respectively. The *N*-cyanoimides (I) give exclusively the 2-chloro-4-amino-pyrimidines (IV), but with the dithio-



SCHEME 1

carbonate (II) the isomers (IV) and (V) (R¹ = MeS) are obtained in 2:3 ratio in 88% total yield. Representative overall yields and m.p.s of the pyrimidines (IV) are, for R¹ =

Me, 87%, 254 °C; Et, 83%, 232 °C; Prⁿ, 83%, 199 °C; Buⁿ, 85%, 185 °C. The structure of (IV; R¹ = Me) was established by reaction with ethanethiol to the known 4-amino-5-cyano-2-ethylthio-6-methylpyrimidine.³ Allenstein and Fuchs⁴ have recently prepared the 5-cyanopyrimidines (IV; R¹ = NH₂) and (V; R¹ = OEt) by an analogous ring closure.



SCHEME 2

The reaction with ethyl cyanoacetate (Scheme 2) provides a new route to the uracils. Representative overall yields and m.p.s of the uracils (VIII) are, for R¹ = Me, 90%, 350 °C; Buⁿ, 85%, 281 °C; MeS, 88%, 299 °C. This method should be preparatively useful since there are few routes to 5-cyanouracils.⁵

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¹ K. R. Huffman and F. C. Schäfer, *J. Org. Chem.*, 1963, **28**, 1816; W. Lwowski, *Synthesis*, 1971, 263. The aliphatic *N*-cyanoimides (I) are obtained in 70–80% yield by treatment of the corresponding imido ester hydrochloride with cyanogen chloride and Et₃N in Me₂CO-CHCl₃.

² A. Hantzsch and M. Wolvekamp, *Annalen*, 1904, **331**, 282. The potassium salt of cyanoimidodithiocarbonic acid was methylated in high yield with Me₂SO₄ in water.

³ R. G. Jarque and C. V. Sala, *Anales fis. y quim.*, 1946, **42**, 349.

⁴ E. Allenstein and R. Fuchs, *Chem. Ber.*, 1968, **101**, 1244, and references therein.

⁵ G. Shaw, *J. Chem. Soc.*, 1955, 1834; H. Meindl and H. Ackermann, *Helv. Chim. Acta*, 1972, **55**, 1039.