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SECONDARY AMINES FROM CYANAMIDES : A NEW METHOD FOR REMOVING THE -CN GROUP

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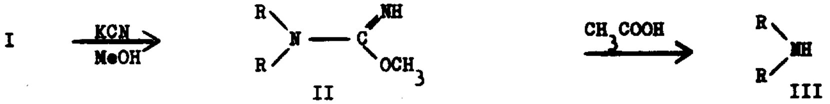
The preparation of secondary amines from cyanamides is a well known method (1). However, in our attempts to prepare some secondary terpenylamines, this method failed to give good results. Actually, the saponification of the intermediate disubstituted cyanamides according to the usual procedures (1,2,3,4,5) is too drastic, leading to double bond migrations and decomposition products.

We wish, now, to report a new particularly mild procedure for converting disubstituted cyanamides to secondary amines. In addition, we have developed a suitable modification of the customary synthesis of cyanamides, by reacting the corresponding halides (2 mole) with Na_2NCN (1 mole) (from H_2NCN and sodium methylsulfinylmethide (6)) in DMSO. Unlike the classical procedure (1), in which the cyanamides are prepared by refluxing 2.5 hr the halides with Na_2NCN (from CaNCN and NaOH) in aqueous ethanol, the reaction was more quickly performed at room temperature (0.5 hr) to give (I) in satisfactory yields and without allylic rearrangements :

I

Cyanamides were saponified to amines through a two steps sequence involving the intermediate O-methylisoureas (II). By refluxing in methanol over 24 hr equimolar quantities of I and KCN, II were obtained, isolated and purified by distillation. Their structures were confirmed by elemental analytical data, IR and NMR spectra.



II III

a R = $(CH_3)_2C{=}CH{-}CH_2{-}$

b R = $(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}$

c R = $(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}C(CH_3){=}CH{-}CH_2{-}$ (geranyl)

d R = $(CH_3)_2C{=}CH{-}CH_2CH_2{-}CH(CH_3){-}CH_2{-}CH_2{-}$ (citronellyl).

The intermediate O-methylisoureas (II) were readily saponified to the amines (III) by boiling 18 hr with an excess of 80% CH_3COOH.

The results are listed in Table I.

TABLE I*

Structure	I		II		III	
	b.p. °C	yield,%	b.p. °C	yield,%	b.p. °C	yield,%
a	146-8/15 mm	63	142-3/15 mm	75	92-3/15 mm	65
b	96-8/0.15 mm	55	92-4/0.1 mm	63	116-8/14 mm	61
c	166-8/0.08 mm	61	165-8/0.07 mm	76	134-8/0.04 mm	60
d	154-7/0.05 mm	72	147-9/0.03 mm	81	123-5/0.03 mm	71

* All compounds reported here, except IIIa (7) and IIIc (8), were unknown. Their structures were determined by IR, NMR, elemental analyses and by comparison with the literature data, when available.

The method seems to be of general application. It represents a convenient procedure for the synthesis of secondary amines carrying substituents rather sensitive to the strong mineral acids and bases usually employed in direct saponification of the -CN group.

Further investigations of this procedure are now in progress.

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