NOVEL SYNTHESES OF DIHYDROOXAZINES, TETRAHYDROPYRIMIDINES AND TETRAHYDROPYRIDINES FROM ALLENYL NITRILES

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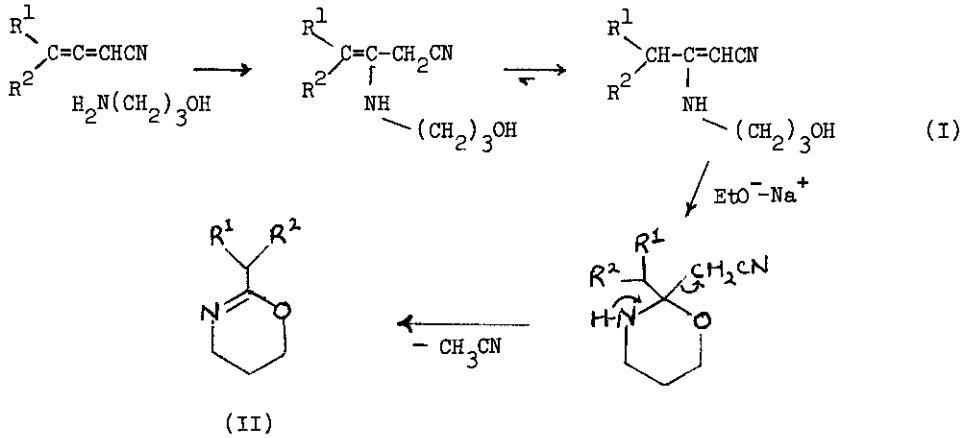
Abstract - α-Allenylnitriles give dihydrooxazines and tetrahydropyridines with 3-hydroxypropylamine whereas with 1,3-diaminopropane they afforded tetrahydropyrimidines.

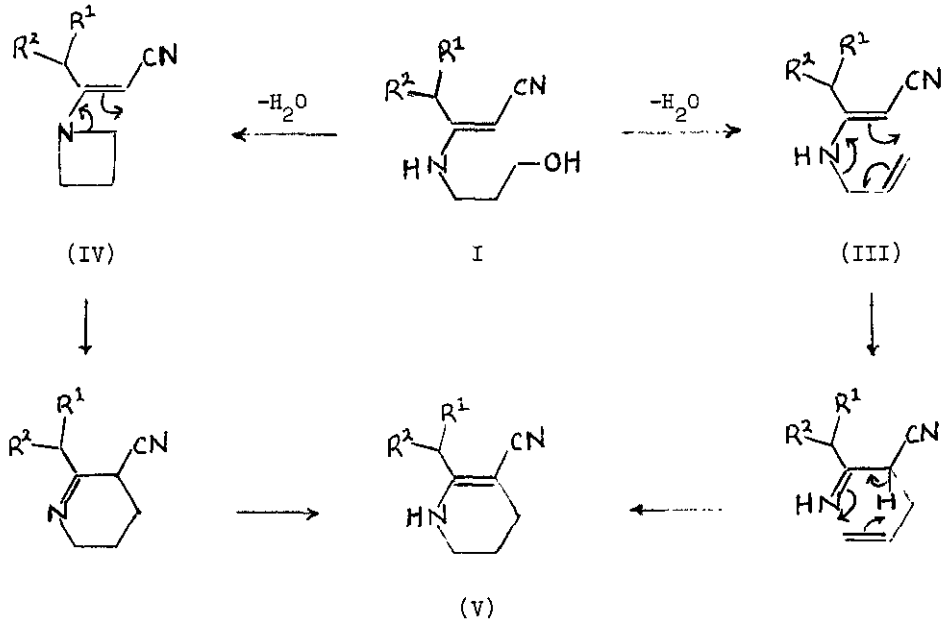
We have previously established that Michael addition of amines to α-allenyl nitriles gives enaminic nitriles in nearly quantitative yields.[1] We now report that the cyclisation of adducts from 1,5-difunctional amines followed by elimination of acetonitrile gives dihydrooxazines (II), tetrahydropyridines (V) and tetrahydropyrimidines (VIII) in good yield.

3-Hydroxypropylamine reacts spontaneously with α-allenyl nitriles to give the enaminic nitriles (I) of 98% purity in quantitative yield. Treatment of (I) with a catalytic quantity of sodium ethoxide and heating at 200-250° effected the Michael type cyclization followed by elimination of acetonitrile to give the dihydrooxazines (II) in 70-75% yield (cf Table).

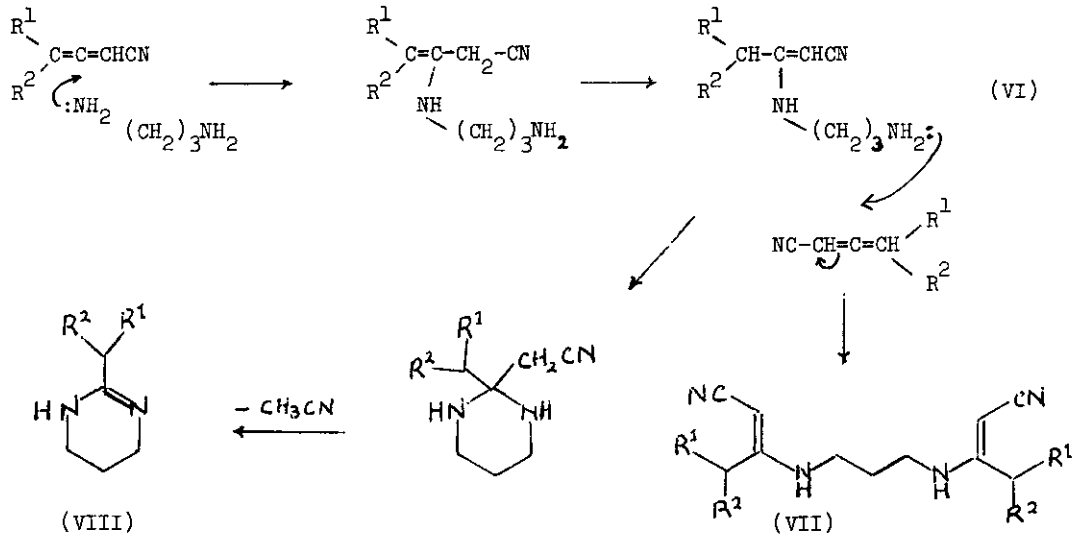


(II)

However, when the enaminic nitriles (I) were heated at 300° in the absence of catalytic sodium ethoxide, in addition to obtaining the dihydrooxazines (II) in ∿30% yield, a second crystalline compound was isolated in 65-70% yield. Elemental and mass spectral analyses show that the latter is derived from the adducts (I) by loss of one molecule of water but does not give signals in the n.m.r. spectrum for olefinic or enaminic protons expected for compound (III). The spectroscopic[2] and analytical data obtained are rationalised by either postulating dehydration of the enamine nitrile (I) to the acetidine (IV) followed by ring expansion[3a] or a [3,3]sigmatropic rearrangement of the N-allylenamine (III) and followed by a concerted sigmatropic ring closure[3b] to give the tetrahydropyridine (V). The two products were readily separated by column chromatography.

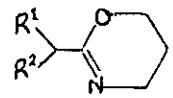
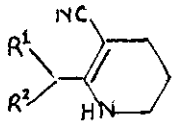
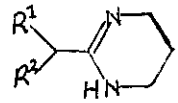
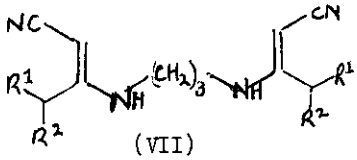


Dropwise addition of allenyl nitriles at 0° to 1,3-diaminopropane gave the Michael adduct (VI) in ∿80% yield and the bis-adduct (VII) in about 20% yield. Thermal cyclisation of the adducts (VI) at 250° gave the tetrahydropyrimidines (VIII) (see Table).



Imidazolines have been obtained from 1,2-diamines and α-allenylnitriles.[4]

Table

	R^1	R^2	b.p.°/760 mm Hg	yield %	m/e
	Me	Et	174	70	141
	Et	Et	190	75	
(II)	Me	Bu^t	220	70	169
			m.p.°		
	Me	Et	115	66	164
	Et	Et	123	68	178
(V)					
			m.p.°		
	Me	Me	38	71	126
	Me	Et	48	86	140
(VIII)	Et	Et	122	81	154
			m.p.°		
	Me	Et	116	17	288
	Et	Et	158	23	316
(VII)					

All heterocycles showed satisfactory elemental analyses and spectral data in agreement with the assigned structures.

References and Notes

1. Z.T. Fomum, P.M. Greaves, P.D. Landor and S.R. Landor, J.C.S. Perkin I, 1973, 1108.
2. Typical spectral data for tetrahydropyridines (IV) are: ν_{max} 2185 cm^{-1}, =CHCN; λ_{max} 280-285 nm, N-C=C-CN; $\tau \sim 5.68$, 1H, broad s, NH exchanges D_2O; 6.79, 2H, m, NH-CH_2-CH_2 collapses to t after D_2O; 7.71, 2H, t, =C-CH_2-CH_2.
3. (a) If concerted the [1,3]sigmatropic ring expansion requires inversion at C2 of the acetidine; (b) [$\sigma 2 + \pi 2 + \pi 2$] sigmatropic reaction.
4. Z.T. Fomum, P.D. Landor and S.R. Landor, J.C.S. Chem. Comm., 1974, 706; Z.T. Fomum, P.D. Landor, S.R. Landor and G.B. Mpango, J.C.S. Perkin I, 1979, 2289.

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