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ALLENIC AMIDES BY HYDRATION OF ALLENIC NITRILES WITH ALKALINE HYDROGEN PEROXIDE AND BY A RITTER REACTION.

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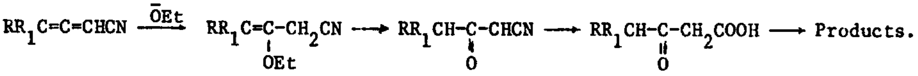
We have recently described general methods for the synthesis of allenic nitriles[1] which rendered these compounds readily available. Some of these nitriles were intended as starting materials for the synthesis of allenic acids, acid chlorides, esters and amides in connection with our programme on biologically active allenes. However, strong nucleophiles preferably attack allenic nitriles in the Michael position (cf formation of enamine nitriles from the reaction with amines[2]) and the usual acid or base catalysed hydrolytic procedures give neither allenic amides nor acids but Michael addition products which often react further to give a mixture of non-allenic products.[3]



$$RR_1C{=}C{=}CHCN \xrightarrow{\bar{O}Et} RR_1C{=}\underset{OEt}{C}{-}CH_2CN \longrightarrow RR_1CH{-}\underset{O}{C}{-}CHCN \longrightarrow RR_1CH{-}\underset{\overset{\|}{O}}{C}{-}CH_2COOH \longrightarrow \text{Products.}$$

In addition the lower homologues (RR_1 = Me or Et) dimerise rapidly at elevated temperatures[4] so that substantial quantities of dimers are found amongst the products. We now describe two exceptions, the reaction of allenic nitriles with alkaline hydrogen peroxide and the Ritter reaction, which result in addition to the cyanide group rather than Michael addition in the 3-position. The addition of hydrogen peroxide (100 vol) to a solution of 4,4-dialkylbutadienenitriles in alcoholic sodium hydroxide gives rise to a vigorous exothermic reaction which is completed by maintaining the reaction mixture at 80° for 1 h. On cooling, the amides crystallize from solution in 60-70% yield[5] (table).

Similarly, in the Ritter Reaction, the addition, with cooling, of allenic nitriles and t-butyl alcohol to a 20% solution of sulphuric acid in glacial acetic acid and leaving overnight, gave crystalline t-butylamides in about 60% yield (table).

In both cases, concerted addition to the nitrile group may account for the specific attack and the absence of Michael addition products. Both types of amides showed an NH stretch band near 3400, ($CONH_2$ showed a second NH stretch near 3200) an allene band near 1960, twin amide bands between 1600 and 1675 cm^{-1} and a signal in the n.m.r. near $\tau 4.5$ for the allenic hydrogen, and all gave satisfactory elemental analyses.

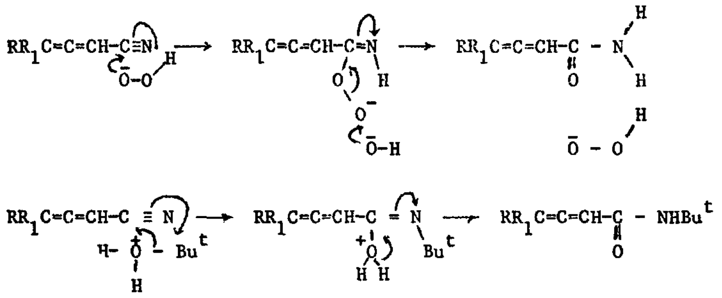


Table.

Synthesis of Allenic Amides from Allenic Nitriles.

$RR_1C{=}C{=}CH{-}CONHR_2$

R	R_1	R_2	%Yield	m.p. °C	λ_{max}^{EtOH} nm	ε
Me	Et	H*	90+	102	210	14,800
Et	Et	H	57	139	208	14,600
Pr^i	Pr^i	H	70	113	210	15,000
Bu^t	Me	H	70	105	209	13,000
Bu^i	Bu^i	H	41	94	211	10,140
Bu^t	Bu^t	H	70	96	208	8,150
Pr	H	Bu^t	55	138	212	19,760
Me	Et	Bu^t	60	140	213	14,700
Et	Et	Bu^t	59	105	214	14,600
Bu^t	Me	Bu^t	61	121	214	13,800

*Cooled during addition, reagents kept at room temperature for 15 min. + yield of crude product.

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[3] cf nueclophilic addition to allenic esters, G. Eglington, E.R.H. Jones, G.H. Mansfield, and M.C. Whiting, J. Chem. Soc. 1954, 397.

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