

DIPOLAR CYCLOADDITION REACTION OF C-ACETYLNITRILE IMINE
WITH ALDONITRONES

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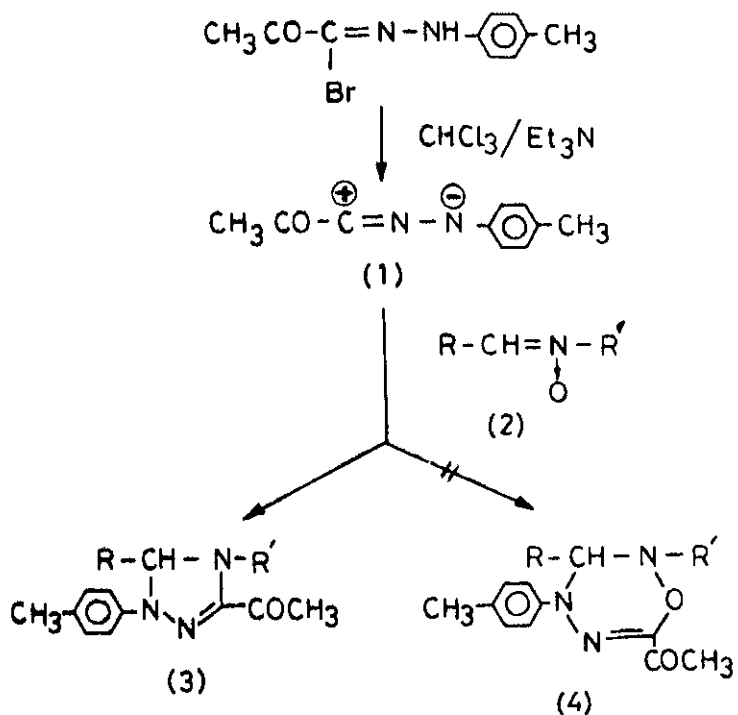
Abstract - 1,2,4- Δ^2 -Triazolines have been obtained in good yields by reacting aldonitrones and C-acetylnitrile imine.

The 1,3-dipolar cycloaddition reactions appear to be a single magic methodology which does not have any other comparable powerful tool for the synthesis of complex heterocyclic molecules¹. Nitrile imines behave as typical 1,3-dipoles and their reactions with a variety of multiple as well as heteromultiple bonds have been extensively investigated². Recently it has been reported that nitrile imine (1) is more reactive than their corresponding aromatic counterpart, diphenylnitrile imine³. Nitrones are also well known dipoles⁴, herein we report their abnormal behaviour, 'aldonitrones (2) when reacted with (1) triazolines (3) were obtained in good yields'.

When (1), generated in situ from the corresponding hydrazonyl bromides (0.01 mol, 2.55 g) in the presence of dry triethylamine (0.02 mol, 2.02 g) in anhydrous chloroform (30 ml), reacted with aldonitrone (2a) (0.01 mol, 2.23 g) 1,2,4- Δ^2 -triazoline (3a), mp 124-126°C was obtained in 61% yield. Similarly were prepared compounds (3b-f) in satisfactory yields. These triazolines have also been obtained in comparable yields by reacting (1) with (2) under two phase system using TEBA (Triethylbenzylammonium chloride) as a phase transfer catalyst and 25% NaHCO₃ solution as a base. Interestingly diphenylnitrile imine generated under similar condition did not participate in this cycloaddition reaction.

Regarding the mechanism of this reaction it is difficult to say anything conclusively accept it is clear deoxygenation of (2) has occurred affording triazolines by the 1,3-dipolar cycloaddition of (1) onto azomethine bond of (2). However it is possible deoxygenation might have simultaneously occurred during

the formation of (3). There was no evidence for the formation of (4). However further work is in progress to establish the mechanism of the reaction.



3	R	R'
a	 -CH=CH	
b	 -CH=CH	
c	 -CH=CH	 -CH ₃
d		
e		

Table : Physical Data of 1,2,4- Δ^2 -Triazolines (3a-e)*.

Product 3	Yield (%)	Yield in two phase system.	Mp (°C)	Conditions time (h)	Molecular formula	Recryst. solvent
a	61	71	124-26	10	C ₂₅ H ₂₃ N ₃ O (381)	Pet. ether
b	62	69	137-38	9	C ₂₃ H ₂₁ N ₃ O ₂ (371)	Pet. ether
c	60	70	135-36	14	C ₂₄ H ₂₃ N ₃ O ₂ (385)	n-hexane
d	61	73	112-13	16	C ₂₁ H ₁₉ N ₃ O ₂ (345)	n-hexane
e	63	72	134-36	18	C ₂₃ H ₂₁ N ₃ O (355)	Pet. ether

* All the compounds reported here gave satisfactory spectral as well as microanalytical data.

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