1,3-DIPOLAR CYCLOADDITIONS OF NITRILE IMINES WITH ALDAZINES

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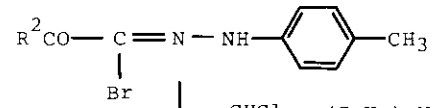
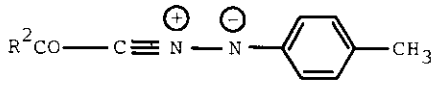
Abstract —— C-Acetyl and C-ethoxycarbonyl nitrile imines reacted with various aldazines and yielded 1,3-dipolar cycloadducts (3) in good yields. Their structures were fully established with the help of spectral analyses and finally structure (3a) was confirmed by X-ray crystallography.

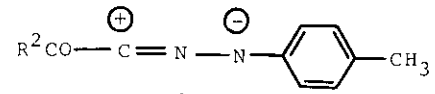
Nitrile imines are well-explored dipoles[1] and their reactions with various multiple bonds are fully investigated. Diphenyl nitrile imines, one of the classical member of this group, are less reactive in comparison to their non-aromatic counterpart, C-acetyl and C-ethoxycarbonyl imines, but are more thoroughly investigated. The reactions of these dipoles with imines and conjugated imines have also been reported.[2] The reaction with aldazines which is the subject of this communication does not appear to have been investigated.

Reaction of C-acetyl nitrile imine (1a) with aldazine (2a) was carried out by dissolving their equimolar amounts in dry chloroform and stirring the reaction mixture at room temperature. The removal of solvent gave a residue which was dissolved in benzene and thus precipitated triethylamine hydrobromide was filtered off and the solvent was removed under reduced pressure. The product (3a) thus obtained was purified by column chromatography and recrystallised from petroleum ether. Similarly compounds (3b-e) were prepared in 60-75% yield and their characteristics are recorded in the table.

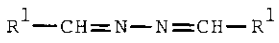
Aldazine could respond as 4π component thereby yielding [4+3] type of cycloadduct[3]







(1)



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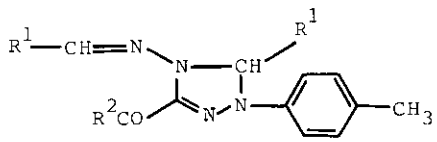

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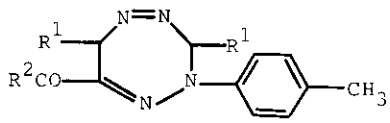
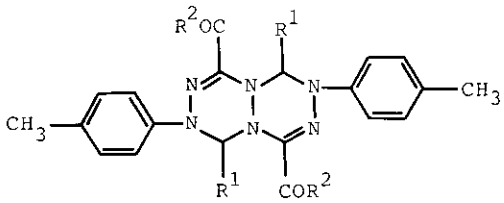
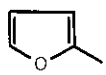
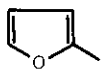
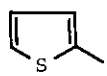
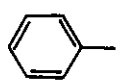
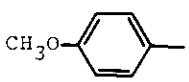


(4)

or



(5)

3	R^1	R^2
a		CH_3
b		OC_2H_5
c		CH_3
d		CH_3
e		CH_3

(4). Also, they are well known to afford 'criss-cross' type of addition products[4] (5). We did not encounter any of these products and the structure of (3a) is supported by microanalytical and spectroscopic data.

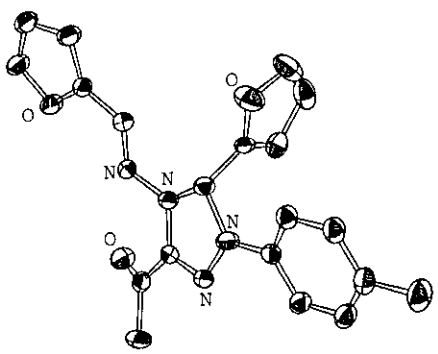
The (3a) was subjected to X-ray analysis[5] to unambiguously confirm the structure.

Table. The Yields, Melting Points and Spectral Data of Triazolines (3a-e).

3*	MP °C	Yield %	MS (M^+) m/e	H^1 NMR (60 MHz, $CDCl_3$) δ ppm
a	117-119	80	362	2.20 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 6.20-7.40 (m, 9H), 7.65 (s, 2H, furan), 7.60 (s, 1H)
b	113-114	60	392	1.21-1.60 (t, 3H, CH_3), 2.25 (s, 3H, CH_3), 4.20-4.61 (q, 2H, CH_2), 6.31-7.55 (m, 11H), 7.80 (s, 1H)
c	126-128	62	394	2.25 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 6.70-7.41 (m, 11H), 8.25 (s, 1H)
d	99-100	75	382	2.15 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 6.35-7.55 (m, 15H), 7.70 (s, 1H)
e	174-175	60	442	2.20 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 3.80 (s, 6H, OCH_3), 6.25-7.55 (m, 13H), 7.70 (s, 1H)

* All the compounds reported here gave satisfactory elemental analyses.

Molecular Structure of the Adduct (3a)



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5. Triclinic, space group $P\bar{1}$ with a=5.353 (3), b=11.576 (1), c=9.201 (3) Å; α= 99.64 (2), β=107.05 (2), γ=99.66 (2)°; Dcalc=1.32 $g \cdot cm^{-3}$ for Z=2. Final R value was 0.090 for 2411 effective reflections.

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