

REACTION OF 1,2,4-TRIAZINES WITH NITRONATE ANIONS, DIRECT NUCLEOPHILIC
 ACYLATION OF 1,2,4-TRIAZINES.¹

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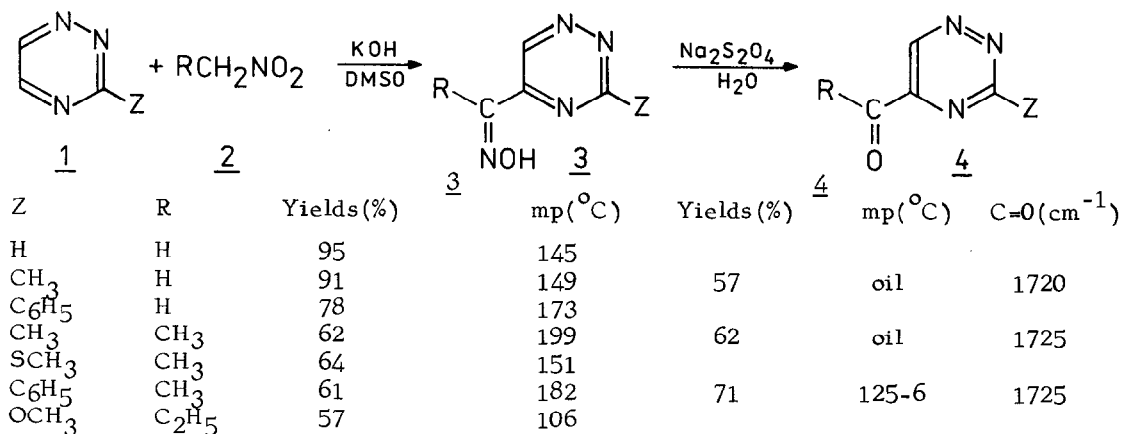
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Summary: Nitronate anions replace 5-hydrogen atom in a variety of 3-substituted 1,2,4-triazine derivatives giving oximes of 5-formyl and 5-acyl 1,2,4-triazines.

Direct replacement of hydrogen in nitroarenes² and some electrophilic aromatic heterocycles³ in reactions of carbanions $R\bar{C}XY$ proceeds easily via the vicarious nucleophilic substitution, which is a general reaction concerning both aromatic electrophiles and carbanions. The latter, however, must contain a nucleofugal group X, acting in this reaction as vicarious leaving group. In the present paper we wish to report an alternative process in which 5-hydrogen atom in 1,2,4-triazine derivatives 1 can be efficiently replaced by α -(hydroxyimino)alkyl substituent via reaction of 1 with nitronate anions. Synthetic value of reactions of nitronate anions with various electrophilic partners (aldehydes, ketones, Michael acceptors, alkylating agents etc) is well recognized.⁴ On the other hand there are only very few reports concerning the reactions of these anions with electrophilic arenes.⁵

We have found that nitromethane and some other primary nitroalkanes react with 1 in the presence of an excess of powdered potassium hydroxide in DMSO to form oximes of 5-formyl- and 5-acyl-1,2,4-triazines 3, scheme and table 1. The oximes 3 are usually produced in good yields and can be easily isolated. They can be cleaved by sodium dithionite to the respective carbonyl compounds (examples given in table), thus the reported reaction can be considered as a direct nucleophilic acylation of 1,2,4-triazines in which nitronate anions 2 serve as nucleophilic acyl group equivalent ($R-CH=NO_2^- = R-\bar{C}=O$).

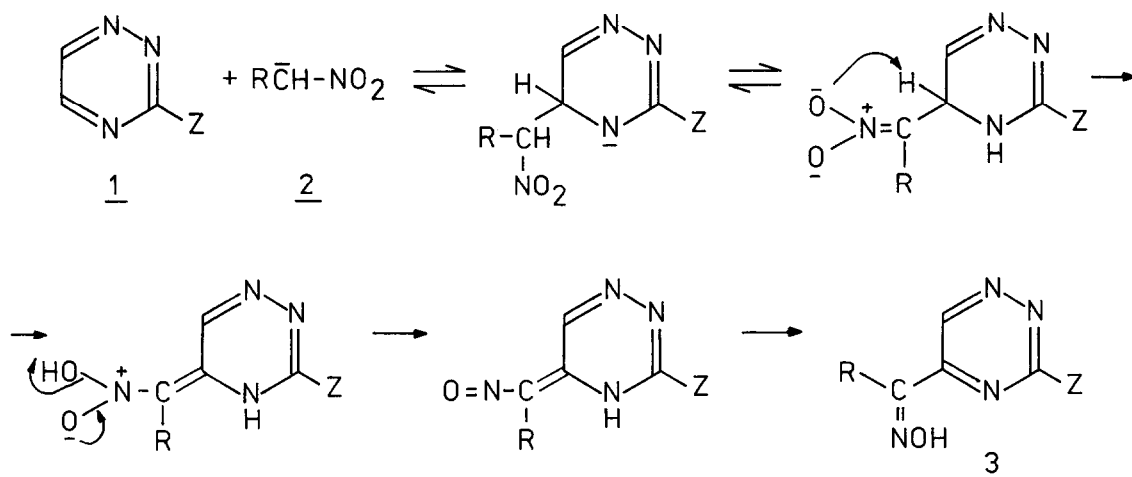
Scheme and table 1



All compounds gave satisfactory elemental analyses.

Transformations of anionic σ -complexes formed via addition of carbanions to carbon atoms of nitroaryl or heterocyclic rings bearing hydrogen to stable products have been observed to occur in a variety of ways: the vicarious substitution (via β -elimination of HX)⁶, oxidation with external oxidants⁷, redox stoichiometry involving the nitro group⁸ or another group present in the electrophile.⁹ Here, we report the first example of a process of redox stoichiometry involving the nitro group located in the nucleophilic partner - nitronate anion.

The mechanism of this interesting process is not clear so far. It seems that the initially formed σ -complexes are converted to the products along the pathway shown below.



Results of further studies on the scope and the mechanism of this reaction will be published in the future.

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