

In order to investigate the generality of this mechanism in the 1,2,4-triazine series, we extended our amination studies to some derivatives containing different leaving groups at C-3 and various substituents at C-5 or C-6 of the triazine ring (see Figure).



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|--|-----------------------|--------------------|---|-----------------------|---------------------|
| 1. X = F | R ₁ = Ph | R ₂ = H | 11. X = SCH ₃ | R ₁ = t-Bu | R ₂ = H |
| 2. X = Cl | R ₁ = Ph | R ₂ = H | 12. X = SO ₂ CH ₃ | R ₁ = t-Bu | R ₂ = H |
| 3. X = Br | R ₁ = Ph | R ₂ = H | 13. X = +N(CH ₃) ₃ | R ₁ = t-Bu | R ₂ = H |
| 4. X = J | R ₁ = Ph | R ₂ = H | 14. X = Cl | R ₁ = H | R ₂ = Ph |
| 5. X = OCH ₃ | R ₁ = Ph | R ₂ = H | 15. X = SCH ₃ | R ₁ = H | R ₂ = Ph |
| 6. X = SCH ₃ | R ₁ = Ph | R ₂ = H | 16. X = Cl | R ₁ = Ph | R ₂ = Ph |
| 7. X = SO ₂ CH ₃ | R ₁ = Ph | R ₂ = H | 17. X = OCH ₃ | R ₁ = Ph | R ₂ = Ph |
| 8. X = +N(CH ₃) ₃ | R ₁ = Ph | R ₂ = H | 18. X = SCH ₃ | R ₁ = Ph | R ₂ = Ph |
| 9. X = Cl | R ₁ = t-Bu | R ₂ = H | 19. X = SO ₂ CH ₃ | R ₁ = Ph | R ₂ = Ph |
| 10. X = OCH ₃ | R ₁ = t-Bu | R ₂ = H | 20. X = +N(CH ₃) ₃ | R ₁ = Ph | R ₂ = Ph |

It was found that besides the corresponding 3-amino compounds as main product, several by-products are formed depending on the nature of the substituents on positions 3 and 5.

With the compounds 2, 3 and 4 a considerable amount of 2,4-diphenyl-1,3,5-triazine is obtained as by-product together with some of the dehalogenated product 5-phenyl-1,2,4-triazine.

With compound 6, ring contraction into 3-methylthio-5-phenyl-1,2,4-triazole takes place as side reaction.

It has been proved using the corresponding [4-¹⁵N]triazines that the formation of the 3-amino compounds occurs by a ring opening - ring closure sequence (S_NANRORC) and/or by the more classical addition-elimination mechanism (S_NAE). As proved by nmr spectroscopy the addition of the amide ion to C-5 in 3-X-triazines is more favoured than addition to C-3. However, in cases where a substituent is present at C-3 which has highly electron-attracting properties [+N(CH₃)₃, SO₂CH₃], the addition to C-3 is the favourite process. The mechanism of the amination and the ring opening process will be discussed.

REFERENCES

1. A. RYKOWSKI, H. C. van der PLAS, *Roc. Trav. Chim.* 94, 204 (1975).

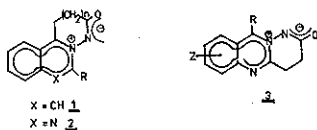
LE 120

SOME NOVEL TYPE ELECTRON DEFICIENT HETEROAROMATIC AMMONIOAMIDATES

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We wish to report on the synthesis of novel type electron deficient heteroaromatic ammonioamidates derived by incorporation of the amidate nitrogen and carbon and of the ammonio nitrogen atoms into a second ring (Compounds 1, 2, 3).

The key step of the syntheses is based on neighboring-group participation of the nitrogen atom of the starting heteroaromatic system in the cleavage of acyl azide groups.



The structures of 1, 2 and 3 were proved by spectroscopical means and by unambiguous syntheses.

The tautomerism and photochemical behaviour of 1-3 were also investigated.

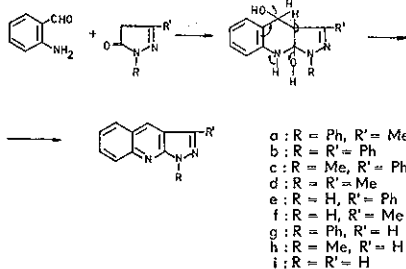
LE 121

THE CONDENSATION OF o-AMINO BENZALDEHYDE WITH PYRAZOLE-5-ONES

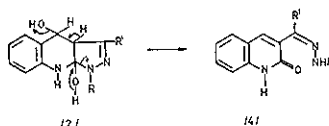
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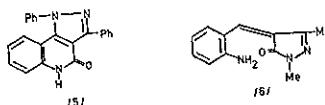
The Friedländer quinoline synthesis was extended to the condensation of o-aminobenzaldehyde with pyrazole-5-one and its derivatives (1a-1i) in order to obtain pyrazoloquinolines (3)



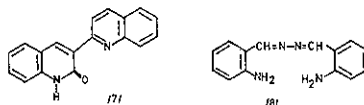
This could be achieved only in few cases. The behavior of the intermediary compound (2) depends on the electronic properties of both the R and R' substituents. When the pyrazole-5-one is not stabilized by R' = Ph the pyrazole moiety in the intermediary compound (2) is cleaved and corresponding hydrazones of 1-H-3-acylquinoline-2-one (4) are formed apart from other products.



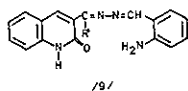
In the case of 1,3-diphenylpyrazole-5-one (1b) pyrazoloquinoline(5) is also formed by the intramolecular Michael-type addition and subsequent oxidation. 1,3-Dimethylpyrazole-5-one (1d) is much more resistant towards condensation and the major product formed was 1,3-dimethyl-4-(o-aminobenzylidene) pyrazole-5-one (6).



Moreover, both hydrazones (4a) and (4d) undergo condensation with o-aminobenzaldehyde yielding 3-(2-quinolyl)quinolin-2-one (7). Also benzylidenepyrazole-5-one (6) turns into both pyrazoloquinoline (3d) and quinolylquinoline-2-one (7). 1-H-Pyrazole-5-ones (1f) and (1i) which are not stabilized with R' = Ph can be a source of hydrazine. The latest is formally liberated from pyrazole-5-ones yielding with o-aminobenzaldehyde 2,2'-diaminobenzaldazine (8).



Corresponding both 3-benzoyl- and 3-formyl-1-H-quinoline-2-ones (4e) and (4i) are also formed, however, they undergo condensation with o-aminobenzaldehyde to give azines (9e) and (9i), respectively.



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REACTION WITH AROYLIMIDODITHIOCARBONATE

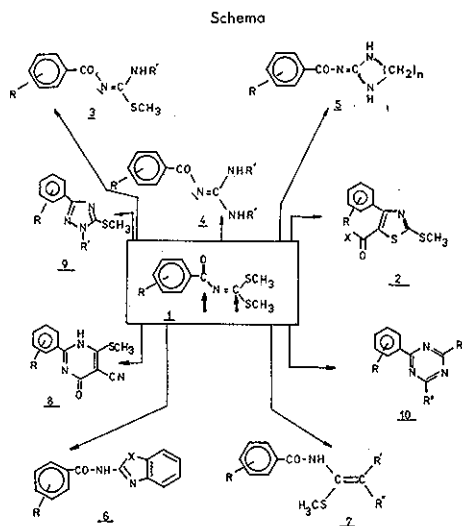
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Abstract — This paper is dealing with the reaction between aroyl-aminodithiocarbonates and alkylating reagents forming aroyl-imidodithiocarbonate 1 and -thiazoles.

The reactivity of these compounds have been investigated. Reaction of 1 with nucleophilic compounds gives new possibilities of synthesizing heterocycles.

With ammonia, aliphatic and aromatic amines 1 yields subst. isothioureas and subst. guanidines. ¹H-NMR spectra of these compounds are interpreted as to their E/Z isomerism and their imine-enamine tautomerism. Reaction of 1 with diamines and aromatic amines, respectively, which still have a nucleophilic substituent in ortho-position next to the amino group leads to the heterocycles. The reaction 1 with CH-acid compounds leads to acylthioamides, with cyanacetamide to the pyrimidone, and with hydrazines, guanidines or thioamides to the heterocycles 1,2,4-thiazole and 1,3,5-triazines.

The mass-, IR- and ¹H-NMR spectra of the synthesized compounds are discussed.



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LE II 1

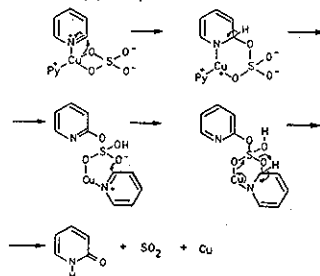
THE OXIDATION OF PYRIDINES WITH COPPER SULFATE

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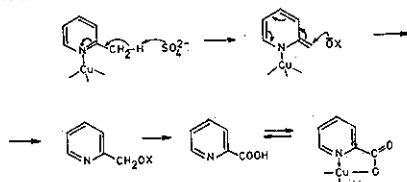
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Oxidation of pyridine, 3-picoline, 3,5-lutidine, quinoline, isoquinoline and acridine with hydrated copper sulfate gives the corresponding pyridones probably via the intramolecular reaction of a base — Cu (II) complex:



The homologues of pyridine bearing the methyl groups in the α- and γ- positions undergo demethylation. The reaction goes via the aldehyde and carboxylic acid formation. Picolinic acid could be isolated after oxidation of 2-picoline owing to the formation of a relatively stable copper chelate. Also 1,2-bis (3-methyl-4-pyridyl)ethylene is formed with a low yield from 3,4-lutidine. Oxidation of the α- and γ- methyl groups may be taking place via the hydrogen — abstraction from the side-chain.



The unusual oxidation of not only the α- but also the β-carbon atom in 2- and 4- ethylpyridines has been discovered. Apart from pyridine also 2- and 4-picolines are formed. As far as we are aware this is the only example known of such an oxidation at the terminal atom of a side chain, containing more than one carbon atom. A radical process seems likely to be involved in this case.

LE II 2

NEW REARRANGEMENTS OF N-CONTAINING RINGS

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