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).

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_2CH_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 = I	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_2CH_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_2CH_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-^{15}N]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 [$+N(CH_3)_3$, SO_2CH_3], the addition to C-3 is the favourite process. The mechanism of the amination and the ring modifying process will be discussed.

REFERENCES

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

LE I 20

SOME NOVEL TYPE ELECTRON DEFICIENT HETEROAROMATIC AMMONIOAMIDATES

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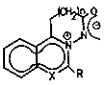
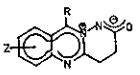
We wish to report on the synthesis of novel type electron deficient heteroaromatic ammonioamidates derived by incorporation of the amidate nitrogen and carbon and of the ammonio nitrogen atoms into a second ring (Compounds **1, 2, 3**).

They 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.



X = CH **1**
X = N **2**



3

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 I 21

THE CONDENSATION OF o-AMINOBENZALDEHYDE WITH PYRAZOLE-5-ONES

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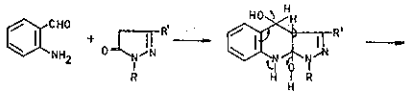
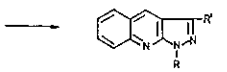
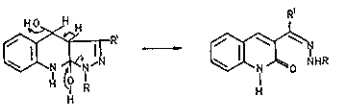
The Friedländer quinoline synthesis was extended to the condensation of o-aminobenzoldehyde with pyrazole-5-one and its derivatives (1a — 1i) in order to obtain pyrozoloquinolines (3)





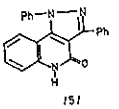
a : R = Ph, R' = Me
b : R = R' = Ph
c : R = Me, R' = Ph
d : R = R' = Me
e : R = H, R' = Ph
f : R = H, R' = Me
g : R = Ph, R' = H
h : R = Me, R' = H
i : R = R' = H

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.

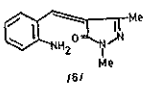


(2) (4)

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).

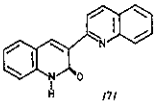


(5)

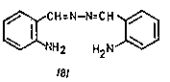


(6)

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).



(7)



(8)