Tetrahedron Letters,Vol.23,No.29,pp 2985-2986,1982 0040-4039/82/292985-02$03.00/0
Printed in Great Britain

REACTION OF 2-FUNCTIONALIZED PYRYLIUM SALTS WITH AMIDRAZONES

P.Molina*,A.Tárraga,M.Lorenzo Peña,E.Hurtado and M.J.Vilaplana

Departamento de Química Orgánica. Facultad de Ciencias.
Universidad de Murcia. Murcia. España.

Summary. A number of derivatives of the bicyclic 1,2,4-triazolo [1,5-a] pyridine (3) and pyrido [2,1-f] [1,2,4] triazine (4 and 7) have been prepared by reaction of 2-methylthio- and 2-ethoxicarbonyl-4,6-diphenylpyrylium salts, respectively, with amidrazones.

The resurgent interest in the chemistry of pyrylium and pyridinium salts is evidenced by the recent review about such compounds[1].

It has been previously shown that N^3-aryl-substituted amidrazones react with triphenylpyrylium to give pyridinium salts which can be converted to carbodiimides[2], while unsubstituted amidrazones lead to the bicyclic pyrazolo [1,5-a] pyrimidines[3].

In this preliminary publication we wish to report the reaction of 2-functionalized pyrylium salts, type 1a and 1b, with N^3-aryl-substituted and unsubstituted amidrazones 2a and 2b.

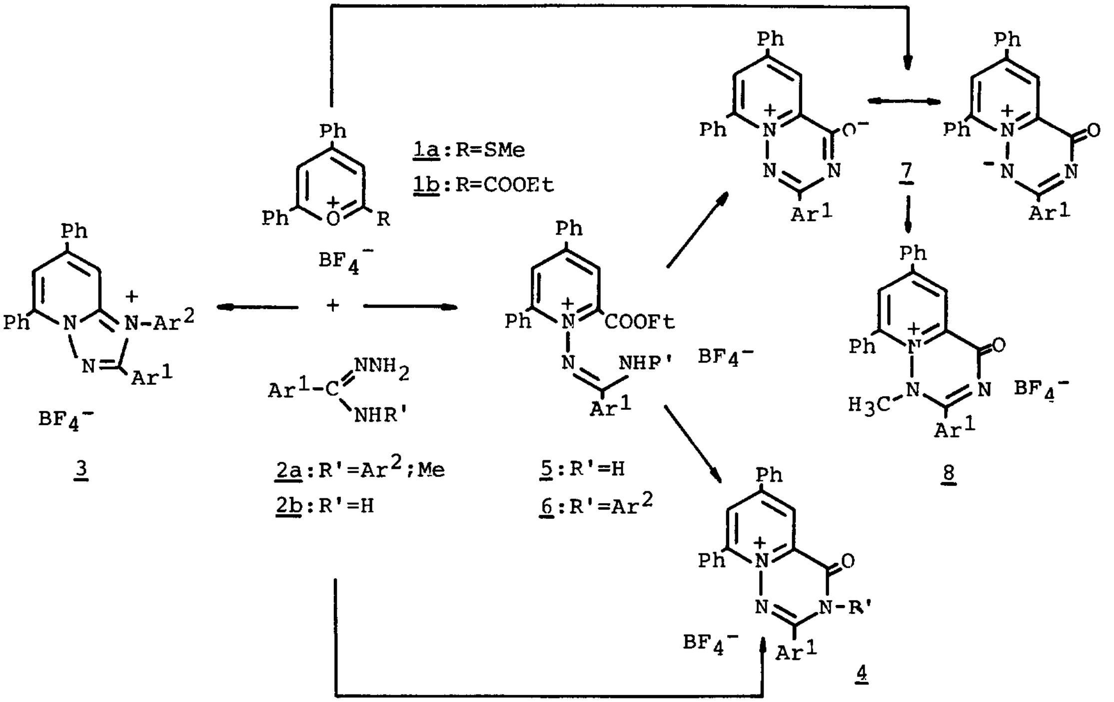
Compound 1a, readily available from 4,6-diphenylpyran-2-thione and trimethyl oxonium tetrafluoroborate, reacts with N^3-aryl-substituted amidrazones 2a in dry acetonitrile to give the corresponding 1,2-diaryl-5,7-diphenylpyrido [1,5-b] [1,2,4] triazolium salts 3 in excellent yields. Support for the formulation 3 is clearly provided by their i.r., n.m.r. and mass spectra. The i.r. spectra of 3 show a strong absorption at 1640 cm^{-1} which can be attributed to C=N stretching. The n.m.r. spectra do not show signals of pyridinium ring protons; mass spectra show the expected ion peak at (M-F$_4$BH) and the base peaks occurs at M-Ar^{1}CN.

Compound 1b, available from ethyl pyruvate, benzalacetophenone and boron trifluoride etherate[4], reacts with N^3-aryl-substituted amidrazones 2a in acetonitrile or methanol at reflux temperature to give the corresponding bicyclic derivatives 4 in good yields. When the reaction is carried out in methanol at room temperature for a short period of time (5 min.) the reaction product is found to be the pyridinium salt 5, which undergoes easily cyclization to 4. The n.m.r.

spectra of 4 show two doublets at δ 8.5 ppm (J=2Hz) attributable to the pyridinium ring protons, and the i.r. spectra show a strong absorption at 1720-1730 cm^{-1} corresponding to the C=O stretching vibration.

Similarly, compound 1b reacts with unsubstituted amidrazones 2b in methanol at room temperature to give the pyridinium 6 in moderate yields. When the reaction is carried out in the presence of triethylamine the bicyclic derivative 7 is obtained in excellent yields. The i.r. spectra of compounds 6 show an absorption at 1745 cm^{-1} corresponding to ester group, while compounds 7 show a band at 1640-1670 cm^{-1}. These latter compounds undergo N-methylation at position 1 by action of Meerwein's reagent to give 8 which show in the i.r spectra absorption at 1710-1725 cm^{-1}, and in the n.m.r. spectra show a singlet at δ 3.3 ppm corresponding to $N-CH_3$ group. The correctness of structure 8 is supported by comparison of m.p. and spectral properties with 4 (R'=Me).

The elemental analyses of all compounds are in good agreement with the proposed structures.



Acknowledgement: We thank Prof. A.R. Katritzky, University of Florida (USA) for his help and comments this paper.

References

1. A.R.Katritzky, Tetrahedron, 36, 679 (1980)
2. A.R.Katritzky, P.L.Nie, A Dondoni and D Tassi, J.Chem.Soc. Perkin Trans. I 1961 (1979).
3. A.R.Katritzky and A.Tárraga Tomás, Heterocycles (in press)
4. A.R.Katritzky, P.Ballesteros, A.Tárraga Tomás, J Chem.Soc. Perkin Trans. I 1495 (1981).

(Received in UK 17 May 1982)