Tetrahedron Letters,Vol.24,No.33,pp 3523-3526,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

FUSED MESOIONIC HETEROCYCLES : SYNTHESIS OF 1,3,4-TRIAZOLO(3,2-a)PYRIDINE DERIVATIVES

P. Molina*, M. Alajarín, A. Arques, R. Benzal and H. Hernandez.

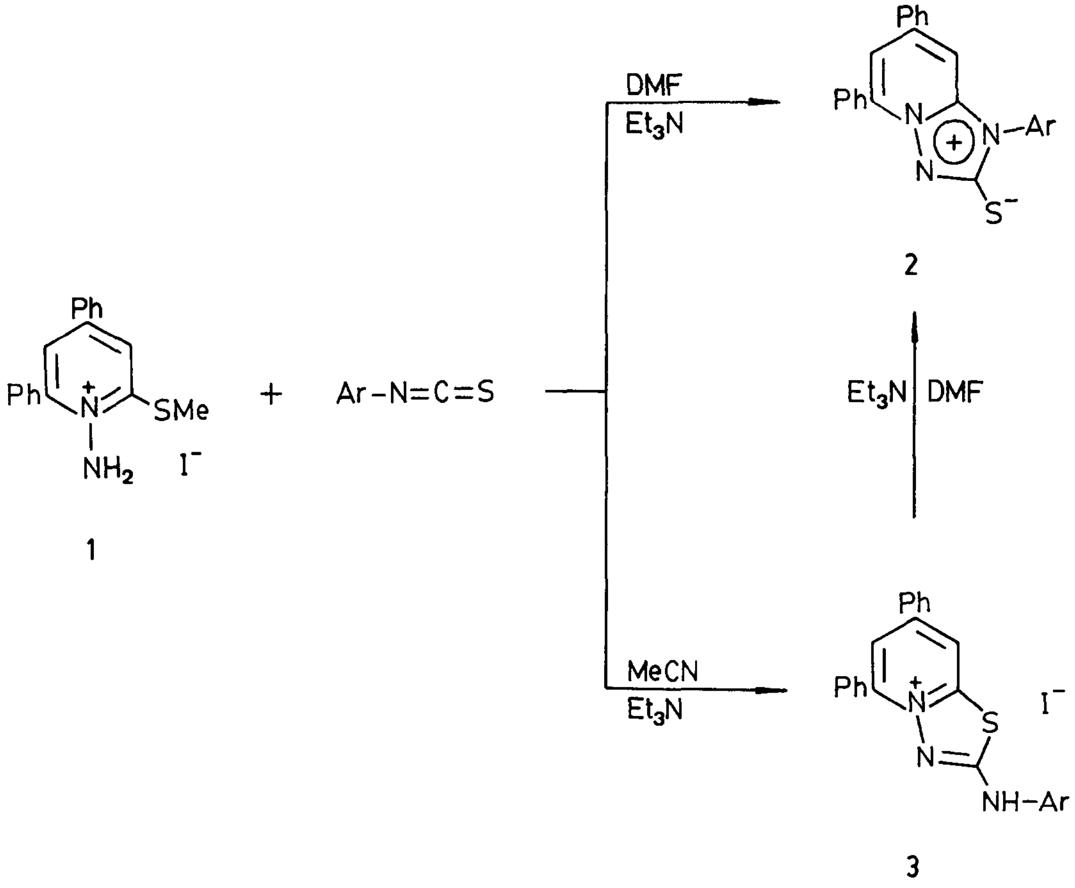
Departamento de Química Orgánica. Facultad de Ciencias.
Universidad de Murcia. Murcia. Spain.

Summary: A number of mesoionic compounds derivatives of the bicyclic system 1,3,4-triazolo(3,2-a)pyridine have been prepared, and an improved method for the preparation of 1,3,4-oxadiazolo(3,2-a)pyridylium-2-aminides from 1,3,4-oxadiazolo(3,2-a)pyridylium-2-olate and iminophosphoranes is described.

Recently we have reported two general methods for the preparation of mesoionic derivatives of 1,3,4-oxadiazolo(3,2-a)pyridine and 1,3,4-thiadiazolo (3,2-a)pyridine from 1-amino-4,6-diphenyl-2-pyridone and 1-amino-4,6-diphenylpyridine-2-thione respectively[1,2]. We report here attempts to synthesize 1,3,4-triazolo(3,2-a)pyridylium-2-thiolates and 2-aminides.

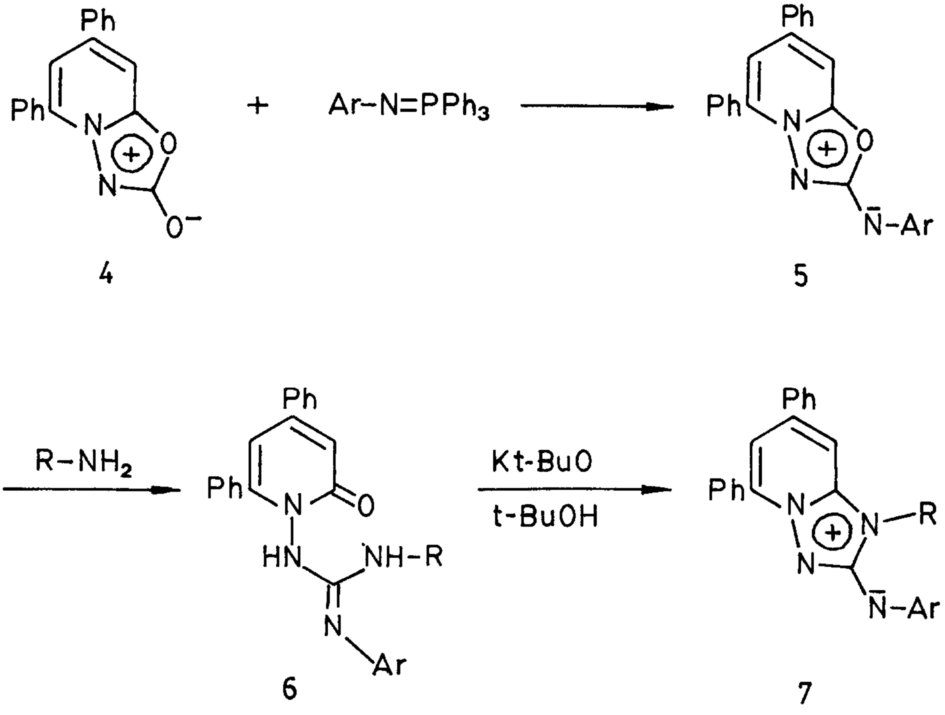
1,3,4-Triazolo(3,2-a)pyridylium-2-thiolates.

1-Amino-4,6-diphenyl-2-methylthiopyridinium iodide (1), readily available from 1-amino-4,6-diphenylpyridine-2-thione and methyl iodide[3], reacts with aryl isothiocyanates in dimethylformamide in the presence of triethylamine at room temperature to yield the new mesoionic compounds 1-aryl-5,7-diphenyl-1,3,4-triazolo(3,2-a)pyridylium-2-thiolates (2) as orange crystals in high yields (2, Ar=Ph; m.p. 125°; 79%). However, when the reaction is carried out in acetonitrile at reflux temperature the previously unreported 2-aryl-5,7-diphenyl-1,3,4-thiadiazolo(3,2-a)pyridinium iodides (3) were isolated as crystalline solids in high yields (3, Ar=Ph; m.p. 298°; 86%). The conversion (3) → (2) is achieved in almost quantitative yield by treatment with triethylamine in dimethylformamide at room temperature. Support for the formulation (2) is clearly provided by their spectral data. Compounds (2) show absorption at 1380 cm^{-1} attributable to C=S stretching which may be compared in position with the thione stretching shown in the monocyclic 1,2,4-triazolium-2-thiolates[4]. Mass spectra of (2) show the expected molecular ion peaks and the fragmentation pattern is similar to the reported for the monocyclic series[5]. Compounds (2) react with methyl iodide to give the corresponding methiodides as crystalline solids (δ_{SMe} 3.5-3.7)



1,3,4-Triazolo(3,2-a)pyridylium-2-aminides.

5,7-Diphenyl-1,3,4-oxadiazolo(3,2-a)pyridylium-2-olate[1] (4), reacts with N-aryliminotriphenylphosphoranes, readily available from amines and triphenylphosphine dibromide[6], in benzene solution to give the corresponding 1,3,4-oxadiazolo(3,2-a)pyridylium-2-aminides (5) in high yields (5,Ar=Ph; m.p. 208°, lit.[1] m.p. 208°; 85%). This type of compounds (5) have been previously prepared by reaction of 1-triphenylphosphinoimino-4,6-diphenyl-2-pyridone with aryl isothiocyanates[1,2]. Compounds (5), react with amines in toluene solution at reflux temperature for 24 h giving the new guanidine derivatives (6) as crystalline solids in high yields (6, Ar=Ph, R=PhCH$_2$; m.p. 192°; 84%), which undergo base-catalysed cyclization by action of potassium t-butoxide in t-butanol solution at reflux temperature for 24 h to give the corresponding 1-substituted 5,7-diphenyl-1,3,4-triazolo(3,2-a)pyridylium-2-aminides (7) as orange crystals in high yields (7, Ar=Ph, R=PhCH$_2$; m.p. 274°; 87%). The i.r.



spectra of the new compounds (7) show strong absorption in the region 1550-1570 cm^{-1}, which can be attributed to C=N stretching[7]. The mass spectra show the molecular ion as base peak.

Dipole moments of (2, Ar=Ph) (9.6 D) and (7, Ar=Ph, R=$PhCH_2$) (8.4 D) in benzene solution have been measured and are similar to the analogous monocyclic systems[8]. The u.v. absorption spectra, $\lambda_{max.}^{EtOH}$/nm (ε) 2, Ar=Ph : 262 (20600); 7, Ar=Ph, R=$PhCH_2$: 257 (55600), are also similar to the monocyclic systems[4,7].

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

Acknowledgement: The authors are indebted to Comisión Asesora de Investigación Científica y Técnica for financial support, project number 0289/81.

REFERENCES:

1. M. Alajarin, P. Molina, Tetrahedron Lett., 1980, 4025.
2. P. Molina, M. Alajarin, A. Arques, R. Benzal, J.Chem.Soc. Perkin I, 351 (1982).
3. A. Arques, P. Molina, A. Soler, M.J. Vilaplana, An.Quim.(C), 77, 248 (1981).
4. W.D. Ollis, C.A. Ramsden, J.Chem.Soc.Perkin I, 633 (1974).
5. W.D. Ollis, C.A. Ramsden, J.Chem.Soc.Perkin I, 645 (1974).
6. L. Horner, H. Oediger, Justus Liebigs Ann.Chem., 627, 142 (1959).
7. W.D. Ollis, C.A. Ramsden, J.Chem.Soc.Perkin I, 638 (1974)
8. R.N. Hanley, W.D. Ollis, C.A. Ramsden, G. Rowlands, L.E. Sutton, J.Chem.Soc.Perkin I, 600 (1978).

(Received in UK 14 June 1983)