PO 20

SYNTHETIC APPLICATION OF PYRIDINIUM ARYLSULFONYLMETHYLIDES

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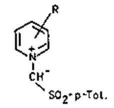
The 1,3 dipolar cycloaddition of pyridinium arylsulfonylmethylides (1) with dimethyl acetylenedicarboxylate has been described recently[1] and led the formation of 1,2-dimethoxycarbonylindolizines (2). Reaction with methyl propiolate gave 1-methoxy carbonylindolizines. 1-Pyridinium arylsulfonylmethylides were generated by deprotonation of the corresponding pyridinium salts. Pyridinium p-toluenesulfonylmethylides also reacted with maleic anhydride in the presence of alcohols to give indolizine-2-carboxylates in a process involving selective decarboxylation and aromatization, and with phenylcyanoacetylene to give l-cyano-2-phenylindolizines.[2]

Rather than expected indolizine derivatives as products of the 1,3 dipolar cycloaddition, reaction of ylide (1). (R = H with N-substituted maleinimides in the presence of nucleophiles R''XH gave[3] compounds (3) involving transfer of a carbon atom from (1) to the maleinimide.

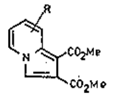
The preparation and the structure of compounds (3) will be discussed in light of spectral measurements and of the physicochemical properties of these compounds.

REFERENCES

1) R. A. Abramovitch and V. Alexanian, J. Org. Chem., 41, 2144 (1976)
2) R. A. Abramovitch and S. S. Mathur, Heterocycles, 5, 91 (1976)
3) R. A. Abramovitch and D. P. Vanderpool, unpublished results.



(1)



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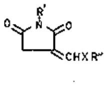

(3)

PO 21

SYNTHESIS OF 1H, 9H-PYROLO[2',3': 4,5]FURO[3,2-b] INDOLE DERIVATIVES

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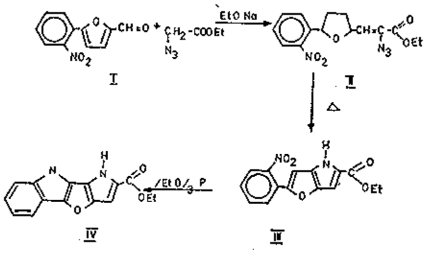
By condensation of 5-(2-nitrophenyl)-2-furaldehyde (I) with ethylester azidoacetic acid was obtained ethyl 3-{5-/2-nitrophenyl/-2-furyl}-2-azidoacrylate (II) which by a thermal ring closure gave ethyl 2-/2-nitrophenyl/-4H-furo-[3,2-b]pyrrole-5-carboxylate (III). Triethyl phosphite deoxygenation of the compound III rendered a derivative of a new heterocyclic system: 1H, 9H-pyrrolo[2',3': 4,5]furo[3,2-b]-indole (IV).



Other convenient way for obtaining of the compound IV is discussed also spectral data of the synthetised compounds are interpreted.

PO 22

SYNTHESIS AND TAUTOMERIC EQUILIBRIA OF 2-METHYLENE -3-OXO-1,2,3,4-TETRAHYDROQUINOXALINE DERIVATIVES

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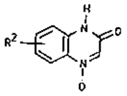
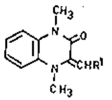
It was found[1] ketimine-enamine tautomeric isomerisation (1) of 2-ethoxycarbonylmethylene-3-oxo-1,2,3,4-tetrahydroquinoxaline (I, $R^1 = CO_2C_2H_5, R^2 = H$) is catalysed with acids. In this paper the measurements of tautomeric equilibria by means of ^1H NMR ($^2H_6$—DMSO, 30—120 °C) was extended to further derivatives of the mentioned ester with substituents in the benzene ring (CH_3, Cl, NO_2, OCH_3) and to the derivatives with another groups activating the tautomeric isomerisation (CO, CN, NO_2).

I

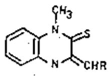
The individual 6- and 7-substituted esters I were prepared[2] using the synthesis via apropriate oxides II (R^2 = 6-or 7-CH_3, Cl, NO_2 OCH_3), wherease the described[3] 6-chloro- and 6-nitroderivatives I ($R^1 = CO_2C_2H_5$, R^2 = 6-Cl or 6-NO_2) were found to be mixtures of both 6- and 7-isomers, their relative amounts were estemated. The cyanoderivative (I, R^1 = CN, R^2 = H) was obtained using a new synthesis starting from 1,2-diaminobenzene and ethyl isoxazole-5-carboxylate as potential α-dicarbonyl compound.



II



III



IV