PO 20

SYNTHETIC APPLICATION OF PYRIDINIUM ARYLSULFONYLMETHYLIDES

R. A. Abramovitch

Department of Chemistry, Clemson University, Clemson S.C. 29631 USA

E. Floch*

Department of Organic Chemistry, Faculty of Chemical Technology, Slovak Technical University, 880 37 Bratislava, ČSSR

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 1-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.

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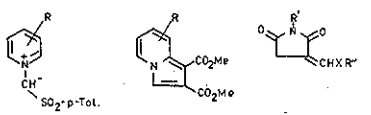
1) R. A. Abramovitch and V. Alexanian, J. Org. Chem., 41, 2144 (1976)
2) R. A. Abramovitch and S. S. Mathur, Heterocycles, 5, 91 (1976)
3) R. A. Abramovitch and D. P. Vanderpool, unpublished results.



(1) (2) (3)

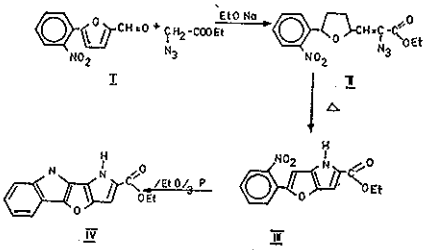
PO 21

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

A. Krutošíková*, J. Kováč, M. Dandárová

Department of Organic Chemistry, Slovak Technical University, 880 37 Bratislava

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).



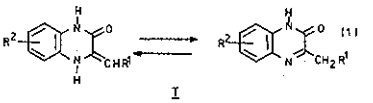
Other convenient way for obtaining of the compound IV is discussed also spectral data of the synthetised compounds are interpreted.

PO 22

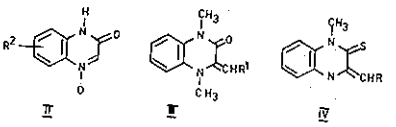
SYNTHESIS AND TAUTOMERIC EQUILIBRIA OF 2-METHYLENE -3-OXO-1,2,3,4-TETRAHYDROQUINOXALINE DERIVATIVES

Jaromír Toman, Jiří Klicnar and Vladimír Macháček
Department of Organic Chemistry, University of Chemical Technology, 532 10 Pardubice — Czechoslovakia

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).



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.



The 1,4-dimethylderivative III (R^1 = CO_2Et, CN) with fixed enamine structure were prepared and theire electronic spectra were discussed in comparism with those of parent derivatives I without the methyl groups.

The action of phosphore pentasulfide on 4-methylderivative of ester I (R^1 = $CO_2C_2H_5$, R_2 = H) in chlorbenzene gave 3--thionderivative IV (R = $CO_2C_2H_5$) with the ketimine structure. The thionation in pyridine solution afforded 1,3-dimethyl-1,2--dihydroquinoxaline-2-thione (IV, R = H).

From the values of relative amounts of both tautomers it follows, that electrone — withdrawing substituents decrease the value K_T = ketimine/enamine, the electrone donors having destabilisation effect on enamine. The effect of groups activating the tautomeric isomerisation and the effect of intramolecular H-bonding are discussed.

LITERATURE:

1. Macháček V., Toman J., Klicnar J.: Coll. Czech. Chem. Commun. — in press.
2. Toman J., Klicnar J., Macháček V.: Coll. Czech. Chem. Commun. — in press.
3. Iwanami Y.: Nippon Kagaku Zasshi 83, 316 (1962); Chem. Abstr. 59, 3919 (1963).

PO 23

SYNTHESIS OF SOME 2-ARYL-2,3-DIHYDRO-1,2,4-TRIAZINO [6,5-b]-INDOL-3-ONES

Jan Slouka, Vojtěch Bekárek and Václav Štemberk

Faculty of Sciences. Palacky University, Olomouc, Czechoslovakia

Coupling of diazonium salts with ethyl 3-indolylcarbamate gives high yields of the corresponding 2-arylazo-3-ethoxy carbonylaminoindoles, which undergo easily thermical cyclization to give the respective 2-aryl-2,3-dihydro-9H-1,2,4-triazino [6,5-b] indol-3-ones or the corresponding 4H-tautomers. The starting carbamate has been prepared by the Curtius rearrangement of 3-indolecarboxylic acid azide. Structure of the prepared 2--arylazo-3-ethoxycarbonylaminoindoles and of 2-aryl-2,3-dihydro-9H-1,2,4-triazino[6,5-b]indol-3-ones were studied by means of IR and ^{1}H-NMR spectroscopy with the use of ^{15}N-labeled derivatives.

PO 24

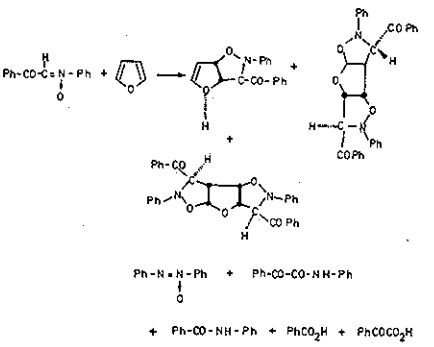
1,3-DIPOLAR CYCLOADDITION REACTION OF C-BENZOYL-N--PHENYLNITRONE WITH FURAN AND ITS DERIVATIVES

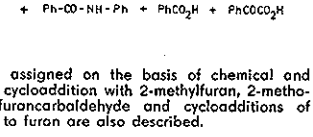
Ľ. Fišera and J. Kovac

Department of Organic Chemistry, Slovak Institute of Technology, 880 37 Bratislava, Jánská 1, Czechoslovakia

A frontier orbital treatment [FMO] of furan suggests its possible reactivity in 1,3-dipolar cycloadditions with dipoles possessing low lying LUMO's, such as nitrones, especially those with electronwithdrawing substituents.

In this lecture is reported a detailed study of the cycloaddition of C-benzoyl-N-phenylnitrone to furan, with particular attention directed at the regiochemistry of the reaction and to the detection of substitution products. On performing the reaction following products were obtained:





The structures were assigned on the basis of chemical and NMR evidence. The cycloaddition with 2-methylfuran, 2-methoxycarbonylfuran, 2-furancarbaldehyde and cycloadditions of some other nitrones to furan are also described.

PO 25

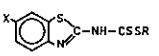
SYNTHESIS AND ANTITUBERCULOTIC ACTIVITY OF S-ALKYL 2-(6-X-BENZOTHIAZOLYL)-DITHIOCARBAMATES

A. Gvozdjaková[a]*, Ž. Odlerová[b], T. Göghᵃ

[a]Department of Organic Chemistry, Faculty of Science, Komensky University, 816 31 Bratislava

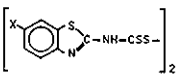
[b]Research Institute of Epidemiology and Microbiology, Department of Tuberculosis, 881 27 Bratislava

The relation between structure and tuberculostatic activity of S-Alkyl 2-(6-X-benzothiazolyl)dithiocarbamates



against M. tuberculosis $H_{37}R_v$ and M. tuberculosis INH resistent has been studied

It has been proved that biological activity of dithiocarbamic groups isn't influenced by the sturcture of used amine. This fact has been also demonstrated on 2-(6-X-benzothiazolyl)thiuram disulphides



It has been stated, that tuberculostatic activity is increased by the substituents in position 6 in this order:

$$NO_2 \rangle Cl, Br \rangle NH - CO - CH_3 \rangle CH_3$$

In this connection the influence of lenght of alkyl R has been studied. The most effective have been found the alkyls C_2—C_5.