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INVESTIGATION OF THE RELATIVE RATE OF NITRATION OF FIVE-MEMBERED HETEROAROMATIC COMPOUNDS BY' THE COMPETITION METHOD

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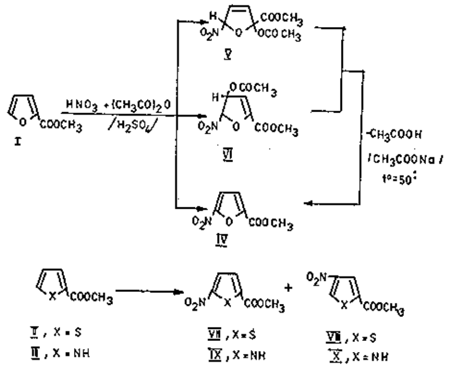
There are some complications with measurement of the reactivity of the furan compounds in the nitration reaction that are due to the low stability of furan ring under strong-acid conditions. Perhaps this is the reason why comparative data on furans and other five-membered heterocycles are not to be found in the literature.

For our investigations we selected a relative acid-resistant compound - methyl 2-furoate (I) which was compared with analogous thiophene and pyrrole derivatives (compounds II and III) in the nitration reaction using the competition method.



Nitration of compound I with acetyl nitrate (formed by the addition of nitric acid to acetic anhydride) gives methyl 5-nitro-2-furoate (IV) and adducts V and VI. The latter are treated with sodium acetate to be converted into compound IV. Analogous nitration of compound II gives a mixture of compounds VII and VIII (in ratio 1,44 : 1) but compound III gives IX and X (in ratio 3 : 1).

The relative reactivity of compounds I—III has beeninvestigated by the method of competition nitrotion using small quantity of nitrating agent. Ratios of the formed nitroproducts give evidence of the relative velocity of the initial attack of the carbon atoms of heterocycles by the active nitrating particle. Separation, estimation and quantitative determination of the starting materials and reaction products have been performed using TLC and GLC. The results of our investigation support such a sequence of relative reactivities of heterocycles: pyrrole 〉 furan 〉 thiophene, which is in good agreement with the results obtained in the investigation of the above heteroaromatic compounds in other electrophilic and radical reactions.

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CATALYTIC SYNTHESIS AND CONVERSION OF HETEROCYCLIC ALDEHYDES

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Aldehydes in the pyridine and diazine series have found wide application as semiproducts in the synthesis and production of medicoments, agricultural chemicals and analytical reagents.

Vapour-phase oxidation of 2-, 3-, 4-mono-, 2,3-, 2,4-, 2,5-, 2,6-di-, 2,4,6-trimethylpyridines, methylpyrazine and 4-methylpyrimidine to the corresponding formyl derivatives was studied at 250—450 °C using vanadium-molybdenum catalysts with various ratios of vanadium and molybdenum oxydes.

Selectivity of aldehydes formation was analysed as to the catalyst composition and reaction conditions. It was found that the highest yield of monopyridinaldehyles could be gained when the catalyst contained mainly the solid solution of MoO_3 in V_2O_5, whereas dialdehyde formation in the reaction of 2,6-dimethylpyridine oxidation was maximal on the vanadium-molybdenum catalysts having predominantly MoO_3 (hexagonal and rhombic forms). On the catalysts containing equal amounts of both oxides maximum yields of diazinaldehydes were obtained. Interaction between methyl derivatives of pyridines and diazines with the active centres on the catalyst surface was studied using IRS, EPR and UVS methods.

It was established that aldehydes are formed on the catalyst surface on heating the adsorbed methylazines in the oxygen. A possible mechanism explaining oxidative conversions of methylpyridines and the corresponding aldehydes on the vanadium-molybdenum catalysts is suggested on the basis of 2-methyl-, 2,6-dimethylpyridines, pyridine-2-carboxaldehyde, 6-methylpyridine-2-carboxaldehyde and pyridine-2,6-dicarboxaldehyde oxidation kinetics data. Parallelconsecutive model is suggested as the most plausible mechanism for the reaction of methylpyridines. On the other hand, oxidation of 2,6-dimethylpyridine to pyridinedicarboxaldehyde proceeds mainly in a consecutive manner via 6-methylpyridine-2-carboxaldehyde.

It is assumed that in the process of methylpyridine and pyridinecarboxaldehyde oxidation different sites of the catalyst are implicated.

The effect of H_2O vapours on the adsorption and oxidation of methylpyridines and pyridinaldehydes on vanadiummolybdenum catalysts was investigated to reveal that water promotes accumulation of pyridinaldehydes, apparently, by inhibiting their consecutive conversions.

Conditions have been worked out for the catalytic synthesis of 2-, 3-, 4-pyridine-, 3-methylpyridine-2-, 4-methylpyridine-2-, 5-methylpyridine-2-, 2-methylpyridine-4-, 6-methylpyridine-2-aldehydes and pyridine-2,6-dialdehyde pyrazinaldehyde and 4-pyrimidinaldehyde by means of vapourphase oxidation of the appropriate methyl derivatives. The present method provides production of the above compounds at the rate of 200 g/l h, with 60—80 % selectivity.