PO 49

NEW RINGTRANSFORMATION OF AS-TRIAZINES

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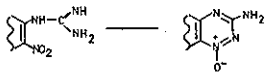
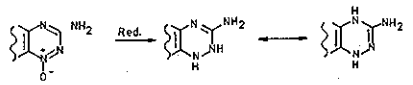
Some as-Triazine (2), condensed with N-heterocyclical ring, were synthetised by o modified method of Arndt[1,2]:



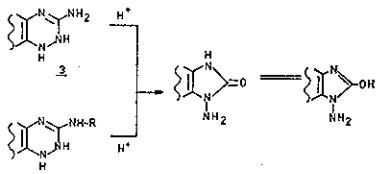
1 2

As-Triazino-(6,5-c)-chinolin and Pyrido-(4,3-e)-as-Triazine-N--oxide were reduced in the presence of sodium dithionit or catalytically and the oppropriate dihydro-as-Triazines (3) could be isolated.



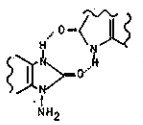
2 3

According to our experiences dihydro-derivates (3) has been showing activity to proton-catolytical rearrangement. Following that the transformation of 3 gave the suitable N-amino-imidazolinon (4), condensed with heterocyclical ring.



3a 4

By preparative way, it had been also proved, that the leaving group which-one nitrogenatom included. Our new compounds were identified from their analysis and spectroscopic properties (IR, NMR). IR-spectra of 4 show the next cyclic-dimer structure (5):



5

We studied also chemical properties of 4 be the reactions of their amino- and oxo-groups.

REFERENCES:

1) E. Berényi; P. Benkó; L. Pallos: Acta Acad. Sci. Hung. 90 (4), 395—97 (1970)
2) P. Benkó; E. Berényi; A. Mossmer; Gy. Hajós, L. Pallos: Acta Acad. Sci. Hung. 90 (4), 405—10 (1976)

PO 50

β-LACTAM ANTIBIOTICS WITH NOVEL RING SYSTEMS

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PO 51

CARBON-13 NMR INVESTIGATION OF 1,2,5-OXADIAZOLE DERIVATIVES

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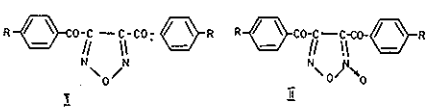
Carbon-13 NMR spectra of 3,4-dibenzoyl-1,2,5-oxadiazole (Ia) and its 2-oxide (IIa) as well as of the corresponding p-methyl and p-methoxy analogs were investigated in a CH_2Cl_2—CDCl$_3$ solution, chromic acetylacetonate being used in order to facilitate assignments of the quaternary carbon atoms.



I II

(a) R=H; (b) R=CH_3; (c) R=OCH_3

In the asymmetric N-oxides (II), the oxide oxygen atom produced magnetic differentiation of the corresponding carbon atoms as between the benzoyl substituents. As expected, the differences in the chemical shifts were rather small; they amounted to 1.32—1.43 ppm for the carbonyl carbon atoms, 0.82—0.94 ppm for the **ortho** carbon atoms, 0.20—0.22 ppm for the **meta** carbon atoms and 0.08—0.17 ppm for the **para** carbon atoms. It is noteworthy that no magnetic non-equivalence was observed for the aromatic carbon atoms in the closest vicinity of the carbonyl group. This may be considered as an indication that the differentiation observed, in particular that pertaining to the aromatic portions of the molecule, originates from the N → O bond anisotropy rather than from inductive and mesomeric effects transferred through the electron system. In each case, lower values of the chemical shifts were noted for the benzoyl moiety juxtoposed to the oxide. In IIb and IIc, the methyl group carbon atoms, sufficiently remote from the anisotropy source, proved magnetically equivalent. The effect of the N-oxide was particularly pronounced in the case of the oxadiazole carbon atoms C(3) and C(4). In Ia, for exomple, the two carbon atoms were equivalent with the chemical shift of 152.86 ppm. In the corresponding N-oxide (IIa), the difference in the chemical shifts was remarkably large (about 42 ppm) owing to the striking upfield shift of the C(3) signal (111.58 ppm as compared with 154.28 ppm for C(4)).