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TAUTOMERIC STRUCTURE AND ALKYLATION PRODUCTS OF 3,5-DIOXO-4-PHENYL DERIVATIVES OF ISOXAZOLE AND PYRAZOLE

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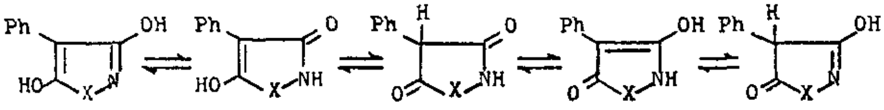
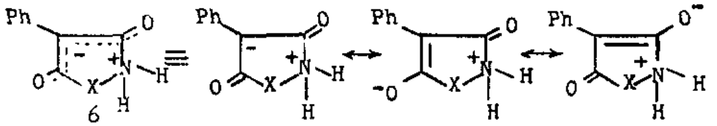
The predominant tautomeric structures of the title compounds were determined by studying the corresponding alkyl derivatives. In addition to the 5 "classic" possible structures (1-5), the "non-classic" tautomer 6 is of particular interest, since the discovery of the stable 4nπ betainic five-membered heterocycles.[1-4]

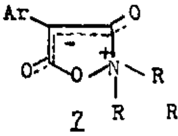


1 2 3 4 5

X=O, NH



6



7 R=CH_3, C_2H_5

The sites of alkylation depend on the conditions and the alkylating agent. N,O-, O,O-, C,O- and C,N-dialkylation products of both the isoxazole and pyrazole derivatives could be obtained by using methyl iodide, diazomethane and "Meerwein reagent" as alkylating agents. Only in the case of the isoxazole derivative (X=O) considerable amounts of the betainic N,N-dialkylation products (7) were obtained. Variable amounts of 7 were obtained by using the three alkylating agents which are mentioned above. The effect of substituents on the phenyl group on the formation of 7 was studied. Compound 7 demonstrates interesting spectral and chemical properties. It forms a 1:2 complex with TCNQ.

The spectral study of the alkylation products shows that the 3,5-dihydroxy structure is predominant in most solvents when X=NH or NR. In the case where X=O the "non-classic" structure (6) is present to some extent.

References: 1. G. Zvilichovsky, Tetrahedron Lett., 1972, 2351. 2. K.T. Potts, S. Kanemasa and G. Zvilichovsky, J. Am. Chem. Soc., 1980 (102), 3971. 3. W. Z Fridrichsen, Naturforsch. B: Anorg. Chem., Org Chem., 1980 (35B) 1002.
4. G. Zvilichovsky and M. David, J. Org. Chem., 1982 (47), 295.