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A NEW TYPE OF MESOIONIC BICYCLIC HETEROCYCLE BASED ON PYRAZOLE

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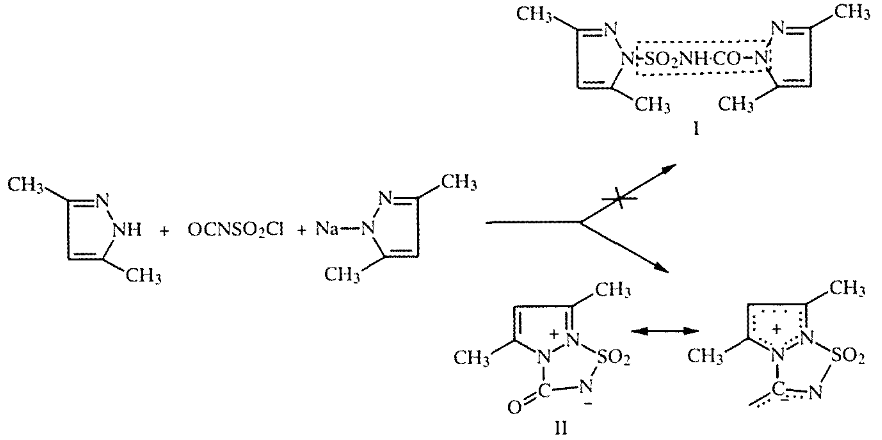
In an attempt to prepare compound I by the interaction of the sodium salt of 3,5-dimethylpyrazole with chlorsulfonyl isocyanate in order to obtain sulfonylureas containing pyrazole rings, we observed that, depending on the reagent ratio, the process gave solely a mesoionic heterocycle II of a new type [1].



Compound II — mesoionic 3,5-dimethylpyrazoli[1,2-*b*]1,2,3,5-thiatrazole-1,1-dioxide-4-ketoamide-5 — is an extremely hygroscopic, rapidly hydrolyzed powder which is somewhat soluble in absolute benzene, dissolves well in absolute acetonitrile and is insoluble in ether and hexane. Since elemental analysis for C, H, N and S gave satisfactory results and that the isocyanate is considerably more reactive than the chlorsulfonyl group towards the NH group [2] any structure for II other than that suggested is unlikely. The ^{1}H NMR spectrum shows unambiguously that the methyl groups of the pyrazole ring remain inequivalent while new characteristic frequencies at 1745 and 1805 cm^{-1} occur in the infrared spectrum, evidently characteristic of this mesoionic heterocycle.

Under conditions excluding moisture, a solution of chlorsulfonyl isocyanate (3.55 g, 0.025 mole) in absolute ether (20 cm^3) was added dropwise with cooling to the sodium salt of 3,5-dimethylpyrazole, prepared from 3,5-dimethylpyrazole (2.4 g, 0.025 mole) and sodium hydride (0.6 g, 0.025 mole) in absolute ether (40 cm^3). The mixture was heated to boiling for 30 min, cooled, and the mixture of sodium chloride and product was filtered off, care being taken to exclude air and moisture. The white powder was treated with boiling absolute acetonitrile (10 min), filtered hot through a sintered glass filter to remove sodium chloride, and the solvent was removed in the absence of moisture to give a light yellow sticky oil (5.0 g, quantitative) which was converted to a white powder by trituration with cold absolute ether.

UV spectrum (absolute ethanol): λ_{max} 218, 248 nm, log ε 3.73, 3.43; (absolute acetonitrile): λ_{max} 218, 249 nm, log ε 3.86, 3.51: Specord M-40. IR spectrum (absolute acetonitrile): 1150, 1290, 1630, 1745, 1805 cm^{-1}; Perkin–Elmer 577. ^{1}H NMR spectrum (absolute CD_3CN): 2.05 and 2.21 ppm (CH_3 groups), 5.97 ppm (4-H); Tesla BS-497 (100 MHz).

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