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1,2,3,5-THIATRIAZOLO [1,2-b] PYRAZOLIUMOLATE-S,S-DIOXIDES. SYNTHESIS AND STRUCTURE OF A NOVEL MESOIONIC SYSTEM[1]

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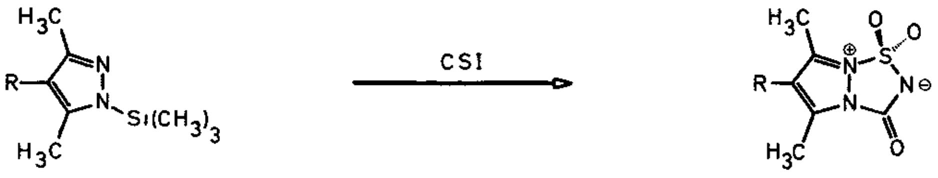
ABSTRACT - The synthesis of the title compounds (2a and 2b) is described. The structure of 2b has been clarified by X-ray crystallography.

Almost all mesoionic compounds - whether they contain five-[3] or six-membered[4,5] heterocyclic rings - carry a carbanion stabilizing group of the type C = X (X mainly O, S, or N-). It is of special interest to know whether such moiety can be replaced by another fragment, e.g. a sulfonyl group. We now succeeded in preparing compounds of this type (2a,b)[6].

Treatment of the activated[8] pyrazoles 1a,b with an equimolar quantity of chlorosulfonyl isocyanate (CSI)[9] in acetonitrile at 0°C under dry nitrogen with subsequent heating to exactly 60°C for one hour, removal of the solvent under reduced pressure, and recrystallization from acetonitrile yields 2a and 2b, respectively.



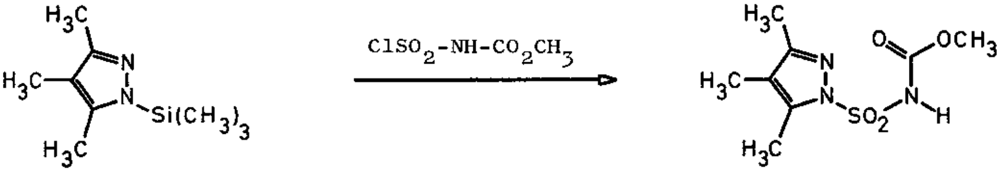
a: R = H ; b: R = CH_3

1a,b

2a,b

2a: 84 % yield, colorless plates with mp 223-225°C dec. - IR(KBr): 1177, 1359, 1743 (w), 1789 (s, sh), 1802 cm^{-1} (s). - ^1H-NMR ($CDCl_3$) : δ = 2.64 (s, 4-CH_3), 2.70 (s, 6-CH_3), 6.40 ppm (s, 5-H). - MS (70eV) : m/e = 201 (M^+, 8%), 95 ($M^{+\cdot}$-$SO_2NCO^\cdot$, 100%). 2b: 91 % yield, colorless prisms with mp 150°C dec. - IR(KBr): 1160 (sh), 1351 (s), 1720 (m, sh), 1763 cm^{-1} (s). - ^1H-NMR($CDCl_3$): δ = 2.07 (s, 5-CH_3), 2.56 (s, 4-CH_3), 2.63 ppm (s, 6-CH_3). - ^{13}C-NMR($CDCl_3$): δ = 7.70 (q, 5-CH_3), 9.81 (q, 4-CH_3), 10.17 (q, 6-CH_3), 141.00 (s, C=O), 141.45 (s, C-4), 142.36 ppm (s, C-6). - MS(70eV):m/e= 215 (M^+, 24%), 109 ($M^{+\cdot}$-$SO_2NCO^\cdot$, 100%).

The hydrolysis of 2a (acetonitrile, equimolar amount of water, RT, 20 min) gives 3,5-dimethylpyrazole sulfate (37 % yield, mp 128-129°C) whereas the methanolysis of 2b (dichloromethane, equimolar amount of methanol, RT, 15 hr) affords 3 (75 % yield, colorless prisms with mp 148.5-149.5°C dec. from acetonitrile. - IR(KBr): 1178, 1382, 1395, 1753, 3485 cm^{-1}. - ^1H-NMR($CDCl_3$): δ = 1.91 (s, 4-CH_3), 2.23 (s, 3-CH_3) , 2.50 (s, 5-CH_3), 3.68 (s, OCH_3), 10.31 ppm (bs, NH)) which can also be obtained in 94%



1b

3

yield from 1b and carbomethoxysulfamoyl chloride (dichloromethane, RT, 30 min)[10,11].

The structure of 2b exhibits some remarkable features. Both the C2 - N3 and N7 - S8 bond lengths are significantly longer than those to be expected for compounds of this type[12,13]. These results, however, compare well with our previous findings for a structurally similar mesoionic heterocycle[2] and are in accord with bond orders resulting from simple HMO calculations[14]. In comparison with an appropriate struc-

Space group: $P2_1/n$
a = 13.374 Å
b = 8.318 Å
c = 8.605 Å
$\alpha = \gamma = 90°$
$\beta = 97.15°$
Z = 4

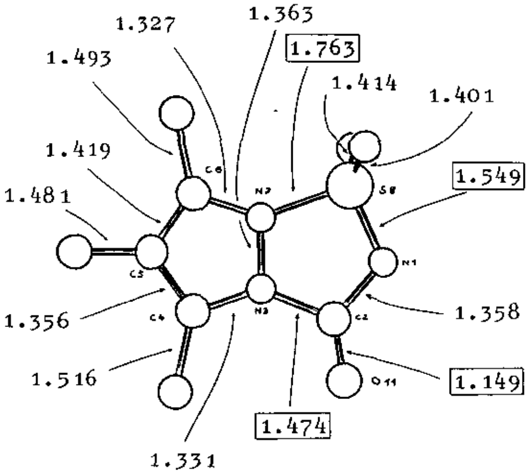


FIG. 1 Crystal Data and Geometrical Data of 2b (X - ray; bond lengths in Å) .

ture moiety of a deprotonated o-sulfobenzoimide[12a], in 2b the N1 - S8 interatomic distance is approximately 0.07 Å shorter (Fig. 1). Additionally the distance between atoms C2 and O11 is even shorter than the corresponding bond length of the mesoionic heterocycle cited above[2]; values in this range, however, are not unprecedented[15].

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