

1,2,3,5-THIATRIAZOLO [1,2-b] PYRAZOLIUMOLATE-S,S-DIOXIDES, SYNTHESIS AND STRUCTURE OF A NOVEL MESOIONIC SYSTEM¹

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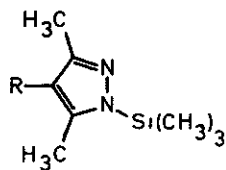
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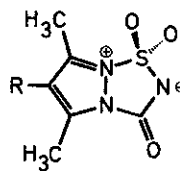
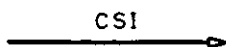
ABSTRACT - The synthesis of the title compounds (2a and 2b) is described. The structure of 2b has been clarified by X-ray crystallography.

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 activated⁸ pyrazoles 1a,b with an equimolar quantity of chloro-sulfonyl 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.



1a,b

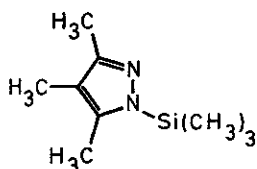


2a,b

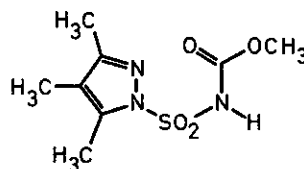
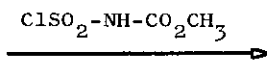
a: R = H ; b: R = CH₃

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(CDCl₃): δ = 2.64 (s, 4-CH₃), 2.70 (s, 6-CH₃), 6.40 ppm (s, 5-H). - MS (70eV): m/e = 201 (M⁺, 8%), 95 (M⁺-SO₂NCO⁺, 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(CDCl₃): δ = 2.07 (s, 5-CH₃), 2.56 (s, 4-CH₃), 2.63 ppm (s, 6-CH₃). - ¹³C-NMR(CDCl₃): δ = 7.70 (q, 5-CH₃), 9.81 (q, 4-CH₃), 10.17 (q, 6-CH₃), 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⁺-SO₂NCO⁺, 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(CDCl₃): δ = 1.91 (s, 4-CH₃), 2.23 (s, 3-CH₃), 2.50 (s, 5-CH₃), 3.68 (s, OCH₃), 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 heterocycle² and are in accord with bond orders resulting from simple HMO calculations¹⁴. In comparison with an appropriate struc-

Space group: $P2_1/n$

$a = 13.374 \text{ \AA}$

$b = 8.318 \text{ \AA}$

$c = 8.605 \text{ \AA}$

$\alpha = \gamma = 90^\circ$

$\beta = 97.15^\circ$

$Z = 4$

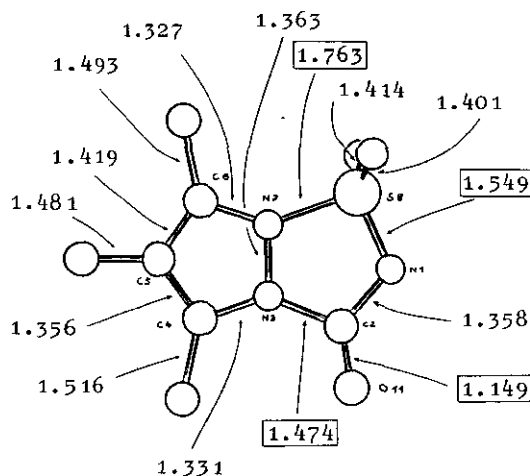


FIG. 1 Crystal Data and Geometrical Data of 2b
(X-ray; bond lengths in Å).

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 above²; values in this range, however, are not unprecedented¹⁵.

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