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3-HYDROXY-PYRAZOLO[1,2-b]1,2,3-TRIAZINIUM-1-OLATES : NOVEL MESOIONIC 10π-SYSTEMS

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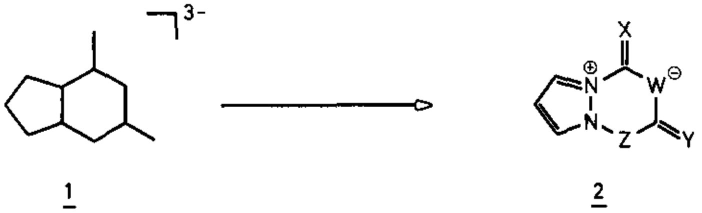
ABSTRACT - The syntheses and reactions of 3-hydroxypyrazolo[1,2-b] 1,2,3-triazinium-1-olates (7a,b) are reported. The structure of 7a has been confirmed by X-ray crystallography.

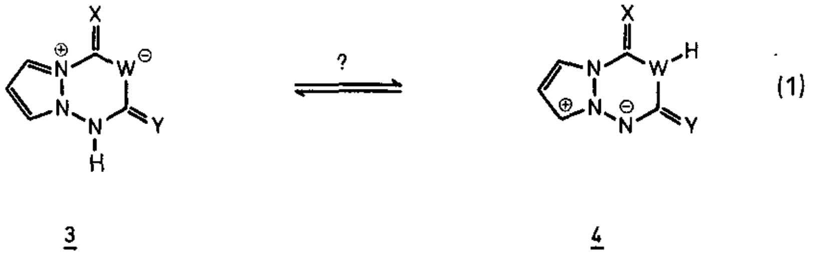
The nonalternant hydrocarbon 1 is the isoconjugate analogue of a new class of bicyclic mesoionic compounds. The introduction of heteroatoms in the depicted sense leads to the novel system 2 which does not seem to have been described until now.



1 2

X,Y,Z : -N,O,S ; W : -C,N

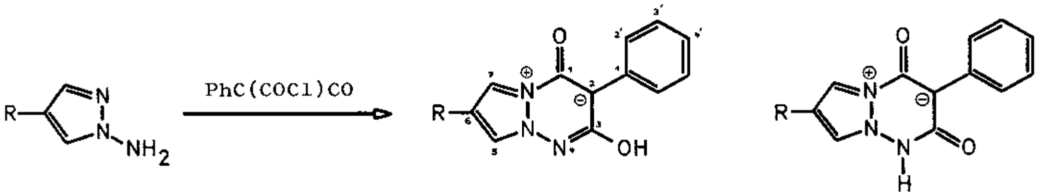
We became interested in compounds of this class firstly, because simple MO calculations (HMO,ω-Technique) predicted unusual bond orders (bond lengths) for these molecules (vide infra) and secondly, because those representatives of 2 with Z = NH could in principle exist (and/or react) either as tautomeric bridged azomethine imines (e.g.(1)) or - as depicted in (2) - as mesomeric 1,4-(5a) and 1,3-(5b) dipoles.



3 4

5a 5b (2)

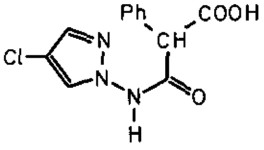
For the present our efforts have been directed on the preparation of compounds of type 3 with W = -C and X = Y = O. Although the starting materials (6a[1], 6b[2]) had been mentioned in literature we were forced to investigate the preparation of these compounds in detail. 1-Aminopyrazole (6a) can be obtained by electrophilic amination of pyrazole with a slight excess of hydroxylamine-O-sulfonic acid in 50 % aqueous potassium hydroxide (15h RT; 42 % yield, colorless oil, bp 85 - 87°C / 30 Torr. - IR (Film): 3115,3130 (CH);3190,3315 (NH_2). - ^{1}H-NMR($CDCl_3$): δ = 5.55 (bs, NH_2), 6.05-6.14 (m, H-4), 7.38 ppm (m, H-3, H-5)), whereas 6b has been prepared from 4-chloropyrazole and H_2NOSO_3H in 1N sodium hydroxide (25-40°C; 71-79 % yield, colorless needles, mp 67-68°C (ether/pentane). - IR(KBr): 3110, 3135 (CH); 3170, 3285, 3310 cm^{-1} (NH_2). - ^{1}H-NMR($CDCl_3$): δ = 5.35 (bs, NH_2), 7.27 (s, H-3), 7.38 ppm (s, H-5)). In strict analogy to the synthesis of malonylheterocycles[3] both 6a and 6b react with chloro-



6a,b 7a,b 8a,b

a : R = H ; b : R = Cl

carbonylphenylketene to give 7a (43 % yield, colorless needles[4], mp 213°C (acetonitrile or acetonitrile/water). - IR(KBr): 1626, 2300-3100, 3121, 3140 cm^{-1}. - ^{1}H-NMR(DMSO-d_6): δ = 7.05 (t, H-6, J=3.1 Hz), 7.13-7.45 (m, 5H, ar-H), 8.45 (d, H-5, H-7, J = 3.1 Hz), 11.25 ppm (s, OH). - ^{13}C-NMR(DMSO-d_6): δ = 85.14 (C-2), 106.71 (C-6), 118.28, 123.22 (C-5, C-7), 125.36 (C-4'), 127.15 (C-3', C-5'), 130.95 (C-2', C-6'), 133.07 (C-1'), 151.85 (C-1), 161.86 ppm (C-3)) and 7b (31 % yield, colorless[4] crystals, mp 208-208.5°C (acetonitrile). - IR(KBr): 1641, 2300-3300, 3155 cm^{-1}. - ^{1}H-NMR(DMSO-d_6): δ = 7.04-7.59 (m, 5H, ar-H), 8.71, 8.82 (d,d, J=1.8 Hz, H-5, H-7), 11.44 ppm (s, OH). - UV(CH_3CN): λ (log ε) = 204.5 (4.44), 244.5 (4.12), 327 nm (4.15))[5]. These data indicate that there are no detectable equilibria between various tautomers. Expectedly 7b is more susceptible to hydrolysis than 7a. On warming in acetonitrile / water (50°C, 10 min) 7b gives a keto acid (9; 100 % yield, colorless needles, mp 133-134.5°C (acetonitrile)) which on heating to the mp looses CO_2 to give 10 (99 % yield, colorless needles, mp 113-114°C (methanol/water)). It is interesting to note that 7a adds tetrachloro-o-benzoquinone under mild conditions (acetonitrile, 40-50°C, 1h) forming 11 (97 % yield, colorless needles, mp 201.5°C (methylene chloride / ether). - IR (KBr) : 1426 (C-O)[6], 1790, 3112, 3120, 3368 cm^{-1} (NH)). The mechanism of this reaction is unknown, but there is no indication that a ketene tautomer of 7a is involved. It may be remarked that other five-[7] and six-membered[8] mesoionic heterocycles show a similar behavior against o-quinonoid compounds (o-quinones, o-benzoquinone-diimines)[9].



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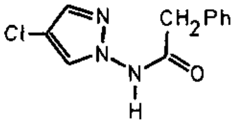

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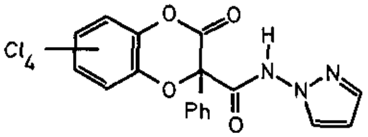

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Simple MO calculations on 7a and 8a reveal a remarkably low bond order between C-1 and N-7a (numbering as in 7)[10]. Therefore it is to be expected that this bond is unusually long. A structure determination of 7a[11] which shows two independent molecules (Fig.1) in the unit cell confirms this result. The C4-O4[13] bond length is comparable with values found for amides[14] and other mesoionic compounds[15] but not with those reported for mesoionic pyrimidinium- and oxaziniumolates[16]. The bicyclic mesoionic system 7a is nearly planar; a maximum deviation from the best plane amounts to 0.07 Å (0.08 Å). The phenyl ring is twisted off from the mesoionic ring by an angle of about 50°, possibly because there is an interaction between O-4, O-6, and H-51, H-55[13]. Similar values have been observed in 4-phenyl-pyrimidinium- and oxaziniumolates[16].

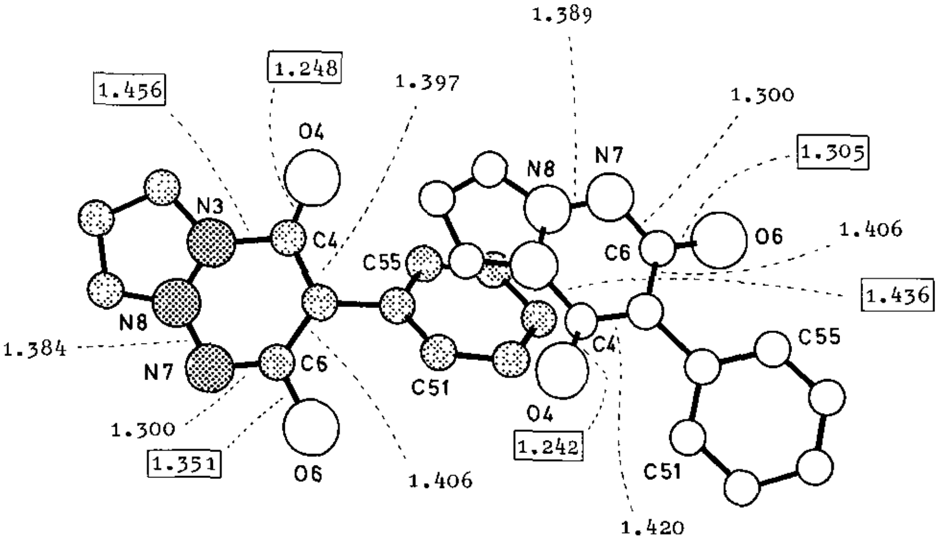

FIG. 1 Geometrical Data of 7a (X-ray ; bond lengths in Å).

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4. We observed two modifications of 7a: modification A with mp 213°C (acetonitrile) and modification B (colorless plates) with mp 204-205°C (IR(KBr): 1591, 1675, 2300-3300, 3110, 3142 cm^{-1}). The ^1H- and ^{13}C-NMR spectra of A and B are identical. - It is to note that even in diffuse daylight both modifications rapidly become yellow. This discoloration was not accompanied by a significant change of the IR-spectra of the substances.
5. The spectroscopic data are not sufficient for a conclusive decision between 7a,b and 8a,b. An X-ray structure determination of 7a shows C6-O6 bond lengths in the C-O single bond region. Therefore we prefer - at least in the crystalline state - formulae 7a,b.
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10. $p_{1,7a}$(7a) = 0.3262 (ω - technique; parameters: F.A.Van-Catledge, J.Org.Chem. 45, 4801 (1981)).
11. Crystal data: $P2_1/c$, $Z = 8$; $a = 13.174(5)$ Å, $b = 12.647(5)$ Å, $c = 12.723(4)$ Å ; $\beta = 90.00(3)^\circ$ [12].
12. The monoclinic space group was choosen because the reflections hkl and $\bar{h}kl$ are not, whereas hkl and $h\bar{k}l$ are equivalent.
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