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SIX-MEMBERED MESOIONIC HETEROCYCLES, VII[1]. SYNTHESIS AND STRUCTURE OF 1, 2, 4, 6-THIATRIAZINIUM-5-OLATE-1, 1-DIOXIDES

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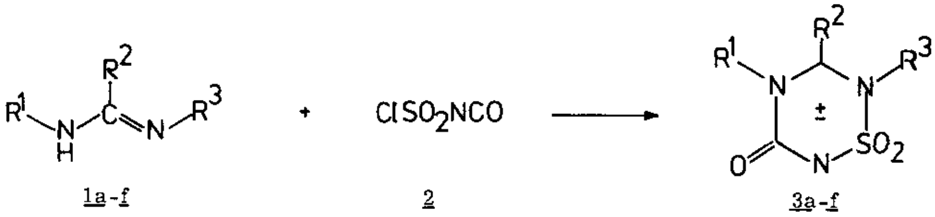
Abstract — The synthesis of 1, 2, 4, 6-thiatriazinium-5-olate-1, 1-dioxides (3a-f) is described. The geometry of 3e has been determined by X-ray crystallography.

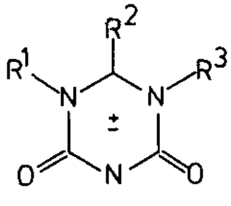
Almost all six-membered mesoionic compounds which could formally be derived from the m-quinodimethane dianion[2, 3], carry a carbanion stabilizing group of the type C=X (X mainly O, S, -N). It would be of interest to know whether such groups could be replaced by SO_2 and how such an alteration influences the properties and the geometry of the heterocyclic system. In a preceding publication we have reported the preparation of a bicyclic five-membered mesoionic[11] heterocycle; in this paper the synthesis of monocyclic mesoionic 1, 2, 4, 6-thiatriazinium-5-olate-1, 1-dioxides (3a-f) will be described.

It is well known[2] that six-membered mesoionic heterocycles of the m-quinodimethane dianion type can be prepared by the reaction of 1, 3-nucleophiles (amides, thioamides, amidines etc.) with 1, 3-electrophiles (reactive malonic acid derivatives, carbon suboxide, phenoxycarbonyl isocyanate etc.). In strict analogy to these syntheses simple amidines[12, 13, 14] (1a-f) react with chlorosulphonyl isocyanate (CSI) (2)[15] in the presence of tert. bases to give the expected heterocycles (3a-f), which can be isolated as colorless, crystalline, high-melting substances. The IR spectra of these compounds show a carbonyl frequency in the region of 1705 - 1720 cm^{-1}. The UV spectra differ from those of 4 in so far as the intensive maxima are shifted hypsochromically[16].

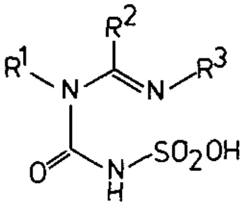
Unsymmetrically substituted amidines may give two isomers of type 3. The reaction of 1e with CSI yielded only 3e; obviously the amino group of 1e reacts - as it is known for other cases - with the isocyanate group of 2 giving an amidosulfochloride, which in the presence of the tert. base is cyclized to 3. The hydrolysis of 3c and 3f (acetonitrile, 2N sodium carbonate, RT) yields the amidosulfonic acids 5c (53%, colorless needles, mp 108°C; IR(KBr): 1185, 1310, 1700, 3220 cm^{-1}) and 5f (55%, colorless prisms, mp 114°C; IR(KBr): 1165, 1365, 1695, 3360 cm^{-1}). Kinetic investigations have shown that the compounds of type 4 are hydrolyzed by a factor of 10^3 faster than compounds of type 3.

The geometry of these new heterocycles is of special interest. An X-ray structure determination





4b



5c,f

1, 3, 4, 5	R^1	R^2	R^3
a	Ph	H	Ph
b	Ph	CH_3	Ph
c	Ph	Ph	Ph
d	CH_3	Ph	CH_3
e	CH_3	Ph	Ph
f	$C_6H_4(4\text{-}OCH_3)$	CH_3	$C_6H_4(4\text{-}OCH_3)$

Table: Spectral Data of 1, 2, 4, 6-Thiatriazinium-5-olate-1, 1-dioxides (3)[a]

3	mp (°C) (yield)	IR(KBr); cm^{-1}	UV(CH_3CN); λ (lg ε)	^{1}H-NMR; δ in ppm (TMS)
a	222(dec) (37 %)	1190, 1335, 1710	235 (4.098)[b], 267 (3.950)[b]	7.51 (s, 5 H), 7.62 (s, 5 H), 8.70 (s, H3))[c]
b	236(dec) (80 %)	1190, 1340, 1705	230 (3.943), 266 (3.493)[b]	1.91 (s, CH_3), 7.52 (s, 5 H), 7.65 (s, 5 H)[d]
c	245(dec) (93 %)	1190, 1330, 1720	231 (4.147)[b], 275 (3.781)[b]	6.9 - 7.6[d]
d	268(dec) (84 %)	1170, 1315, 1705	244 (4.075)	3.01 (s, CH_3), 3.15 (s, CH_3), 7.72 (s, 5 H)[d]
e	257(dec) (99 %)	1185, 1350, 1710	245 (3.979)	3.11 (s, CH_3), 7.17 - 7.52 (m, 10 H)[d]
f	235(dec) (79 %)	1195, 1340, 1720	230 (4.506), 263 (3.805), 278 (3.726)[b]	2.04 (s, CH_3), 3.80 (s, OCH_3), 3.82 (s, OCH_3), 7.0 - 7.65 (m, 8 H)

Footnotes to the table:

[a] All new compounds gave satisfactory analytical data. [b] Shoulder. [c] In CD_3CN.
[d] In DMSO-d_6.

of 3e[18] shows that the N(5) - C(19) and S(1) - N(3) bonds (numbered as in fig. 1) are - expectedly - unusually long (1.489 Å, 1.743 Å), whereas the C(19) - O(2) distance (1.216 Å) is comparable to other simple carbonyl compounds of this type. Remarkably the molecule is not planar. The sulfur atom S(1) appears 0.5867 Å above the N(3) - C(6) - N(5) - C(19) - N(17) plane; the angle between this plane and the N(3) - S(1) - N(17) plane[19] amounts to 145.42°. The influence of a d orbital participation of the hypervalent sulfur[21] upon the geometry and the electronic structure of compounds of this type is open to question.

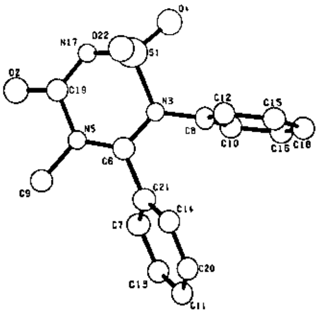


Fig. 1: X-ray structure of 3e

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20. Thanks are due to Dr. C. Ochoa, Instituto de Quimica Medica, CSIC, Madrid, Spain for further details of the X-ray structures reported in this paper.

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