Tetrahedron Letters No. 17, pp 1537 - 1538.
0040-4039/79/0422-1537$02.00/0

THERMOLYSIS OF 6H-1,3,5-OXATHIAZINES
SYNTHESIS OF 3,4-DIHYDRO-2H-1,3,5-THIADIAZINES.

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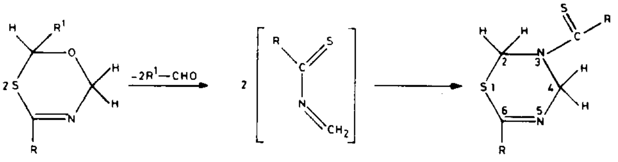
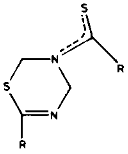
Recently 6H-1,3,5-oxathiazines have been described(1,2,3). At the same time trifluoromethyl and alkyl substituted oxathiazines have been synthesized, by a similar approach, by Burger(1) and by us(2) respectively.

Now we wish to report on the thermolysis of 4-substituted and of 2,4-disubstituted-6H-1,3,5-oxathiazines. Our interest in this topic is related to the synthetic importance of N-thioacylimines(1,4,5), which are supposed to be reaction intermediates in these thermolyses.

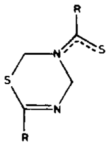
Thermolysis of 4-phenyl-6H-1,3,5-oxathiazine 1a (table) gives 6-phenyl-3-thiobenzoyl-3,4-dihydro-2H-1,3,5-thiadiazine 3a (table).



(1) (2) (3)



"syn"



"anti"

Decomposition via a retro Diels-Alder reaction with formation of the N-thioacylamine 2a (R= C_6H_5), followed by dimerization of 2a (R = C_6H_5) to 3a, via a Diels-Alder mechanism, is a reasonable explanation of these findings. Support for the proposed reaction scheme is given by the thermolysis of oxathiazines 1a-d (R^1=H,CH_3,C_2H_5,C_6H_5), which irrespective of the nature of the substituent R^1 always provides the same thiadiazine 3a together with aldehydes of R^1-CHO type. Similar results have been obtained in the pyrolysis of other oxathiazines (table).

In this connection Burger reported that thermolysis of 2,2,6,6-tetrakis(trifluoromethyl)-4-aryl-6H-1,3,5-oxathiazines leads to 2H-1,3-thiazetes(1). Even if the nature of reaction products differs from that of thermolysis of 2,2,6,6-tetrakis(trifluoromethyl)-4-aryl-6H-1,3,5-oxathiazines(1), it is likely that the decomposition occurs in both cases through the same pathway.

The lack of formation of 2H-1,3-thiazetes is expected both on thermodynamic and kinetic grounds. In fact in the absence of stabilizing groups, such as trifluoromethyl, the formation of thiazetes is very unfavourable(4) while thioacylimines 2 are so reactive that dimerize. To our knowledge only one representative of 3-thioaroyl-6-aryl-3,4-dihydro-2H-1,3,5-thiadiazines has been reported(6).

Structure 3 has been assigned to compounds 3a-d on the basis of their ^{1}H, ^{13}C N.M.R., I.R., and Mass spectral data.

N.M.R. spectral features indicate that compounds 3a-d are present in solution as a mixture of syn and anti isomers.(12)

Table (7) 3,4-Dihydro-2H-1,3,5-thiadiazines 3 from 6H-1,3,5-oxathiazines 1

Starting(8) Material	R	R^{1}	Reaction time(h)	Product	Yield %(9)	m.p. °C(10) (methanol)
1a	C_6H_5	H	3	3a	60	128
1b	C_6H_5	CH_3	3	3a	41	-
1c	C_6H_5	C_2H_5	2.5	3a	61	-
1d	C_6H_5	C_6H_5	2	3a	51	-
1e	$4-H_3C-C_6H_4$	CH_3	3	3b	48	121-123
1f	$4-Cl-C_6H_4$	CH_3	3	3c	81	135-136
1g	$2,6-Cl_2-C_6H_3$	CH_3	2	3d	16	178-180(11) (172-174)(9)

1) K.Burger, R.Ottlinger, J.Fluorine Chem., 11 29(1978) and references cited therein. 2) C.Giordano, A.Belli, Synthesis 789(1975). 3) J.Goerdeler, Tetrahedron Lett.,221(1974). 4) D.S.Blackwell, P.de Mayo, R.Suau, Tetrahedron Lett., 91(1974). 5) K.Burger, R.Ottlinger, Synthesis 44 (1978); K.Burger, R.Ottlinger, Chemiker Zeitung 101, 402 (1977). 6) J.Wijma, J.J. van Daalen, J.Daams, F.W.van Deursen, J.Agr.Food Chem., 18, 674 (1970).

7) Thermolysis of 1a and 1b-g was carried out at 140°/20 torr and at 120°/20 torr respectively; 3a-d were isolated from the residue of distillation via chromatography on silica gel. 8) The synthesis of 1b and 1c has been described previously(2). 1a (oil, purity ≥90%), 1e (m.p. 73-75°, methanol), 1f (m.p. 104-105°, hexane) and 1g (m.p. 82-83°, hexane)were prepared according to the previously described procedure (2) in 30,80,77,77 yield % respectively. 1d (m.p. 67-69°, diethylether at -20°), C.Giordano, A.Belli,to be published. 9) Yield of analitically pure products. All products gave satisfactory microanalyses (C$\pm$ 0.15%, H$\pm$ 0.15%, N$\pm$ 0.10%, S$\pm$ 0.20%).

10) Melting points were determined by the Kofler method and were not corrected. 11) The product crystallizes with a molecule of methanol, which is removed on heating at ~100°C. 12) L.Abis, A.Belli, C.Giordano,to be published.

(Received in UK 27 February 1979)