Tetrahedron Letters No. 48, pp 4629 - 4632, 1971. Pergamon Press. Printed in Great Britain.

THERMOLYTIC DECOMPOSITION OF BENZO-1,2-ISOTHIAZOL-3-ONE-1,1-DIOXIDE (SACCHARIN).

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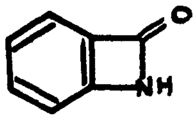
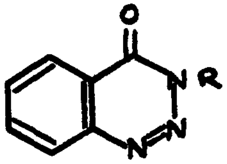
(Received in UK 12 October 1971; accepted for publication 27 October 1971)

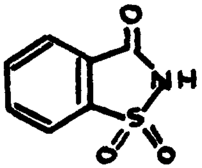
We have recently proposed[1] the intermediacy of benzoazetidone (I) during the thermolysis of benzo-1,2,3-triazin-4-one (II; R = H) in boiling 1-methylnaphthalene. In the search for other potential precursors of (I) the possibility of loss of SO_2 from benzo-1,2-isothiazol-3-one-1,1-dioxide (saccharin) (III) with subsequent formation of (I) became apparent.



I



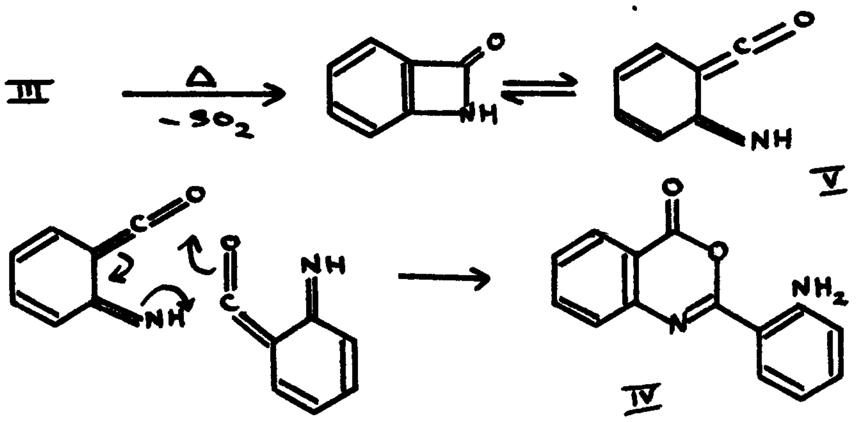
II



III

Saccharin is reported[2] to have a melting point of 228°, but in one instance[3] a melting point of 224° with decomposition has been recorded. We found that saccharin remained undecomposed when heated in boiling 1-methylnaphthalene (b.p. 241-245°) for 15 minutes. Further heating (5 h.) gave unchanged material (80%) together with some carbonaceous products. The mass spectrum of saccharin (parent peak m/e 183), however, showed a loss of SO_2 $(M-64)^+$ as the base peak (metastable at m/e 77.5; calc. m/e 77.35). This result prompted us to investigate the thermolysis of saccharin in solution at higher temperatures.

Accordingly saccharin (2.5 g) was heated under reflux in diethyl phthalate (b.p. 298°) solution for six hours. After removal of starting material (1.5 g.) and excess of solvent, 2-(*o*-aminophenyl)benzo-3,1-oxazin-4-one (IV) was isolated (ca. 5%) by preparative t.l.c. ($SiO_2/CHCl_3$). The formation of benzoxazinone (IV) is readily explained on the basis of a ketenimine intermediate (V) formed by loss of SO_2 from the saccharin molecule. Such an intermediate, which is a valence tautomer of benzoazetidone (I), can as has been shown previously[1], undergo a Diels-Alder type cycloaddition reaction as indicated (scheme) to yield the observed product.



All attempts to improve the yield of benzoxazinone (IV) failed. For example decomposition of saccharin in the absence of solvent at 300+10° yielded only large amounts of tarry material. Similar products were obtained when saccharin was made to decompose in the presence of either copper powder or manganese dioxide. Presumably the low yield of (IV) is a consequence of the high temperature required to bring about decomposition of the saccharin molecule; a factor which can promote competing reactions. In fact we have found that the decomposition medium can alter the manner in which the saccharin molecule fragments. For instance when saccharin was made to decompose in paraffin oil at 300° over six hours, benzamide (ca. 10%)

was obtained. T.l.c investigation of the reaction mixture showed no trace of the aminobenzoxazinone (IV).

Formation of benzamide probably arises by loss of SO_2 from saccharin via a competing radical process which in a hydrogen rich environment (paraffin oil) is preferred and which leads to amide formation by a hydrogen abstraction process. It is of direct interest that a similar reaction has been observed[4] previously during the decomposition of 3-phenylbenzo-1,2,3-triazin-4-one (II; R = Ph). Thermolysis of (II; R = Ph) in paraffin oil at 300° gave benzanilide as a major product, and a radical mechanism was invoked. By comparision we have found that when unsubstitated benzotriazinone (II; R = H) was thermolysed in paraffin oil under similar conditions (300°) or at 240° only the benzoxazinone (IV) was isolated (75%). No trace of benzamide was detected (t.l.c) in the reaction mixture. The difference in the products obtained from the decomposition of benzo-1,2,3-triazin-4-one and the 3-phenyl- substituted compound in paraffin oil may well be accounted for by the enhanced mesomeric stabilisation of the intermediate N-Ph radical involved in the latter instance over that of the NH species involved in the former.

Attempts to bring about the photolytic decomposition of saccharin proved unsuccessful. Irradiation of a solution of saccharin over thirty-six hours in tetrahydrofuran or acetone solution using either a quartz or pyrex filter, gave unchanged material (95%) together with trace amounts of unidentifiable oils.

We thank S.R.C. for a research studentship (A.J.B.) and Professor H. Suschitzky for advice and encouragement.

References

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