Tetrahedron Letters No.53, pp. 5509-5510, 1968. Pergamon Press. Printed in Great Britain.

AN UNUSUAL REARRANGEMENT OF KETOXIME DERIVATIVES +)

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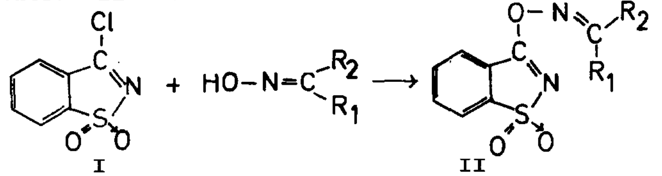
(Received in UK 9 September 1968; accepted for publication 4 October 1968)

3-Chloro benzisothiazole-1,1-dioxide ("pseudosaccharinchloride") I reacts very smoothly with syn-aldoximes and ketoximes to form "pseudosaccharin oxime ethers" II 1).

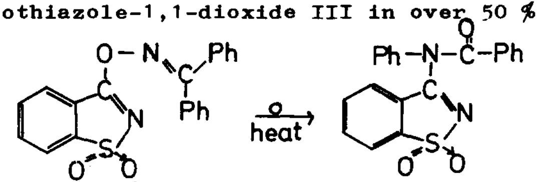

I II

IIa R$_1$=H R$_2$=Aryl
IIb R$_1$=Alkyl, Aryl
R$_2$=Alkyl, Aryl

Under standard conditions 2) the derivatives of ketoximes IIb will undergo BECKMANN-rearrangement. Surprisingly the pseudosaccharin syn-aldoxime ethers IIa on reaction with trifluoro-acetic acid, depending on the nature of substituents R$_2$, yielded the corresponding formanilides HCO-NHR$_2$. Experimental results in the literature on aldoximes and their derivatives seemed to indicate that nitrile formation, which may be followed by hydrolysis was by far the predominant reaction (BECKMANN-fragmentation) 2,3,4).

We now wish to report the result of a thermal rearrangement of pseudosaccharin ketoxime ethers IIb.

Benzophenone oxime ether 1) IIb^1 (R$_1$,R$_2$ = Phenyl) when heated above its melting point (mp. 173°) rearranges to form 3-(N-phenyl-N-benzoyl amino)-benzisothiazole-1,1-dioxide III in over 50 % yield.


IIb^1 III

The structure of III was proved by a simple synthesis. The potassium salt of

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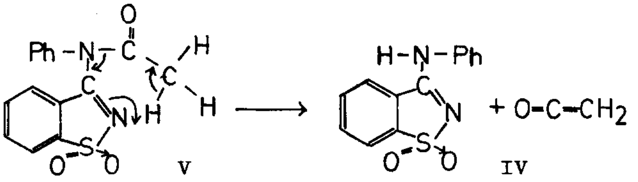
+) Reactions with Pseudosaccharinchloride, Part VI

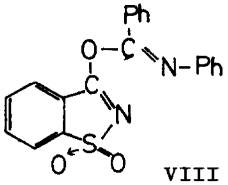
3-anilino benzisothiazole-1,1-dioxide IV ⁵⁾ in pyridine solution was reacted with benzoyl chloride. The resulting product was identical with III in every respect.

III $C_{20}H_{14}N_2O_3S$ mw. 362.39 Anal. Calcd. C, 66.28 H, 3.90 N, 7.73
Found C, 66.50 H, 3.82 N, 7.80

On slow heating the substance melts at 235-241° resolidifies at least partially at 270° and is melted finally at 310-318° (melting point of IV ?). When the pseudosaccharin ether of acetophenone oxime $^{1)}$ VI was heated the isolated product turned out to be 3-anilino benzisothiazole-1,1-dioxide IV. It is conceivable that the expected 3-(N-phenyl-N-acetylamino)-benzisothiazole-1,1-dioxide V undergoes a fragmentation reaction $^{1)}$ with formation of ketene. The experimental proof for ketene formation is still missing.



V IV



VIII

The reported rearrangement bears a superficial resemblance to the formation of N-benzoyl-N,N'-diphenyl benzamidine VII from benzophenone oxime in polyphosphate ester $^{6)}$.

We consider the initial product of BECKMANN-rearrangement VIII as a possible intermediate for the formation of III.

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