Flash Vacuum Pyrolysis of 1,2-Benzoisothiazole 1,1-Dioxides. Benzoxazole and Benzonitrile Formation

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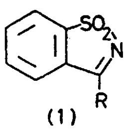
Summary Flash vacuum pyrolysis of 3-aryl-1,2-benzoisothiazole 1,1-dioxides gives mainly 2-arylbenzoxazoles and some benzonitriles, while 3-alkyl-1,2-benzoisothiazole 1,1-dioxides yield principally *o*-cyanophenol; the 3-t-butyl compound gave both benzonitrile and *o*-cyanophenol by preliminary fragmentation to simpler benzoisothiazole 1,1-dioxides.

The flash vacuum pyrolysis (FVP) of 4-phenyl-1,2,3-benzotriazine gives the interesting compound 2-phenylbenzazete.[1] The mass spectral fragmentation of the readily available dioxides (**1**) suggested that 2-substituted benzazetes were important fragments formed in some cases.[2] Since some similarities have been found between FVP and mass spectral fragmentations,[3] we studied the FVP of (**1**).

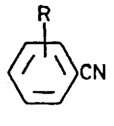
The dioxide (**1a**) was stable at 650 °C but underwent FVP at 850 °C (N_2 flow, pressure 10—15 mmHg during pyrolysis) to give (**2a**) (8%) and (**3a**) (31·7%) which was identical with an authentic sample.[4] No 2-phenylbenzazete was trapped on the cold finger kept at liquid nitrogen temperature. The dioxide (**1b**) similarly gave (**2b**) (6%) and (**3b**) (49·4%).

In contrast, the FVP of (**1c**) gave (**2c**) (54%) but no (**3c**). The FVP of authentic (**3c**) at 850 °C led to recovery of starting material (89%) [(**2c**) was not detected] so that (**3c**) would have been detected readily had it been formed from (**1c**).



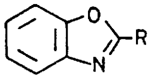
(1)

a; R = Ph
b; R = p-MeC$_6$H$_4$
c; R = Me
d; R = Bu^n
e; R = Bu^t



(2)

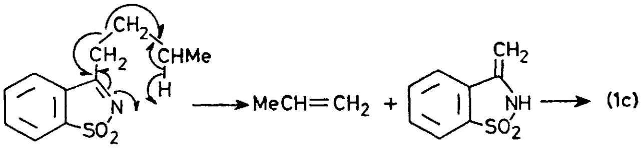
a; R = H
b; R = p-Me
c; R = o-OH



(3)

a; R = Ph
b; R = p-MeC$_6$H$_4$
c; R = Me
d; R = Bu^t
e; R = -CH=CH$_2$

The formation of (**3a,b**) may involve an aziridine intermediate similar to that proposed for the thermal rearrangement of 3,5-diphenylisoxazole to 2,5-diphenyloxazole[5] which would also explain the absence of any 1,2-benzisoxazole in the thermolyses of (**1a,b**). The formation of (**2a,b**) from (**1a,b**) could be explained in a number of ways, one of which is fragmentation to SO$_2$, an aryne, and (**2a,b**), but products derived from the putative aryne were not observed.



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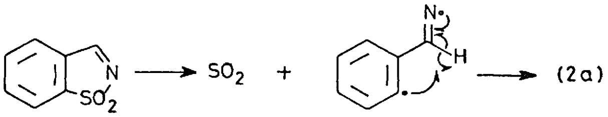
The FVP of (**1d**) gave (**1c**) (4·2%) and (**2c**) (37·5%). Compound (**1c**) could arise by a McLafferty-type rearrangement while (**2c**) could come either from the (**1c**) initially formed or directly from (**1d**). In an attempt to prevent possible hydrogen-abstraction from the α-position of the side-chain, the FVP of (**1e**)[†] at 850 °C was studied. No benzoxazole derivatives were detected in the dark tarry products but (**2a**) (17·1%) and (**2c**) (5·2%) were obtained by preparative t.l.c. Authentic (**3d**)[6] gave (**3e**)[7] (33·8%) together with unchanged (**3d**) (60·3%) on FVP at 850 °C but no (**2a**) or (**2c**). A clue concerning the pathway for the decomposition of (**1e**) is provided by an analysis of its fragmentation pattern on high resolution mass spectroscopy which indicated the formation of the cations of (**1c**), (**1f**; R = Pr^i), and (**1f**): the former two would lead to (**2c**), while (**1g**) would yield (**2a**) [the origin of the benzene ring is necessarily different in this reaction than in the formation of (**2a**) from (**1a**)].



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[‡] M.p. 123—124°; gives expected analytical and spectral data.

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