1,2-Benzisoxazole *N*-Oxides

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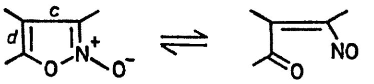
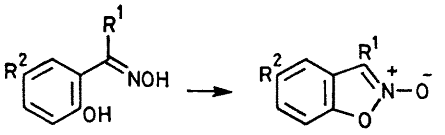
Summary 1,2-Benzisoxazole *N*-oxides are prepared by oxidation of *o*-hydroxyaryl ketoximes with lead tetra-acetate.

ISOXAZOLE *N*-OXIDES are so far unreported in the literature. Kohler[1] in the 1920's prepared a number of 2-isoxazoline oxides, and this system is well established. Tanasescu[2] and Gibson[3] at one time favoured anthranil (2,1-benzisoxazole) N-oxide structures, for compounds which were later shown to be N-hydroxyacridones[4] and benzotriazinone oxides,[5] respectively. One further example, 3-phenylanthranil N-oxide,[6] has not been experimentally disproved, but 2-nitrosobenzophenone, its ring-opened valence bond isomer, is known,[7] and it seems improbable that both compounds are capable of independent existence, at normal temperatures.



(1) (2)



(3); a–f (4); a–f

We reasoned that, if the ring-opening of an isoxazole N-oxide to an acyl-nitroso-olefin (**1**)→(**2**) were to be suppressed, the most likely way to achieve this would be by benzo-fusion to bond *d*, rather than to bond *c*, as in the anthranils, which would, if anything, favour the ring-opened form. Accordingly, we aimed to prepare indoxazene (1,2-benzisoxazole) N-oxides, by oxidation of *o*-acylphenol oximes (**3**). We have found that this reaction is successful when lead(IV) acetate is used, in diethyl ether as solvent. A few examples of indoxazene oxides (**4**) so prepared are tabulated.

TABLE. 1,2-Benzisoxazole N-oxides (**4**).

No.	R^1	R^2	M.p./°C
a	Me	H	96
b	Et	H	37
c	Me	Me	74
d	Ph	Cl	150
e	Ph	Me	90
f	Et	NO_2	127

The products (**4**) are stable crystalline solids. In their mass spectra the parent ions (M^+) are intense; $(M-16)^+$ ions are present, but weak, and $(M-30)^+$ are strong. In this they resemble furoxans, which usually favour loss of NO, rather than O, from the parent ions.[8] The analogy with the furoxans is also seen in the ^{13}C n.m.r. spectra, in which C(3) gives rise to a signal at high field (*ca.* 118 p.p.m.; *cf. ca.* 114 p.p.m. in furoxans)[9].

Some preliminary chemical investigations have been carried out on the N-oxides (**4**). The 3-ethyl compound (**4b**) can be nitrated to form the 6-nitro derivative which is similar to, but not identical with, the 5-nitro compound (**4f**) prepared by cyclisation of the corresponding phenol. Deoxygenation [of (**4a**)] to the indoxazene was successful, but required rather forcing conditions (triethyl phosphite, 113 °C, 45 h, in toluene).

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