Novel Rearrangements of *N*- and α-Halogeno-derivatives of *S*-Aryl-*S*-[(1,2-benzisoxazol-3-yl)methyl]sulphoximides to the Corresponding *N*-Sulphinylimines

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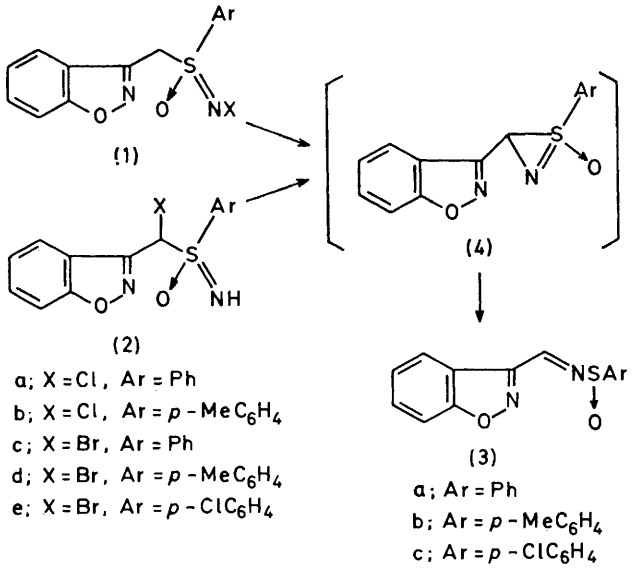
The title *N*- and α-halogeno-sulphoximides (**1**) and (**2**) undergo base-induced rearrangement reactions to give the corresponding *N*-sulphinylimines (**3**), suggesting the intermediacy of a three-membered cyclic sulphoximide (**4**) with an endocyclic S=N moiety.

Much attention has been focused on the synthesis and properties of sulphoximide derivatives which have wide chemical and biological interest.[1] We have previously reported[2] the rearrangement of the *N*-halogeno-*S*-aryl-*S*-[(1,2-benzisoxazol-3-yl)methyl]sulphoximides (**1**) to the corresponding α-halogeno-derivatives (**2**). We now report the novel rearrangement of compounds (**1**) and (**2**) with base to give the same *N*-sulphinylimines, the 3-arylsulphinyliminomethyl-1,2-benzisoxazoles (**3**), suggesting that these rearrangements involve the same intermediate, a thiazirine *S*-oxide (**4**), which



has a novel three-membered ring system with an endocyclic S=N moiety.†

Compounds (**1**) and (**2**) were treated with 1,5-diazabicyclo-[5.4.0]-undec-5-ene (DBU) or potassium carbonate in chloroform or dichloromethane, followed by column chromatography on silica gel with chloroform as an eluant to afford compounds (**3**) as shown in Table 1.

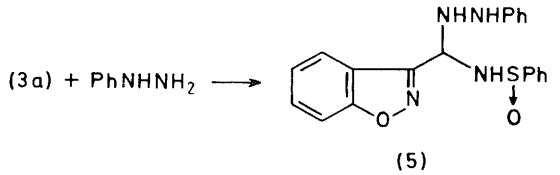
The structure of compounds (**3**) was confirmed by elemental and spectral analyses [*e.g.*, (**3a**): m.p. 135—137 °C; ν 1608 and 1593 cm^{-1} (C=N), 1106 cm^{-1} (SO); δ (60 MHz; $CDCl_3$) 7.2—8.4 (m, 9H, ArH) and 9.28 (s, 1H, CH=N)], and further by the following chemical transformation of compound (**3a**). Thus, reaction of (**3a**) with phenylhydrazine in ethanol gave the adduct (**5**), m.p. 127—131 °C, in 60% yield. The structure

† C. R. Johnson and H. G. Corkins, *J. Org. Chem.*, 1978, **43**, 4140, reported the intermediacy of a three-membered cyclic sulphoximide with an exocyclic S=N moiety in the base-induced Ramberg–Backlund-type reaction of α-halogeno-*N*-(*p*-tolylsulphonyl)-sulphoximides to give alkenes, and also that the reaction of *S*-butyl-*S*-(1-chlorobutyl)sulphoximide with KOH–MeOH gave butane-1-sulphinamide, the production of which could be rationalized in a number of ways, including a three-membered S–N heterocyclic intermediate, but the data were not sufficient for an unambiguous determination of the exact mechanism; the present results seem to support this speculation.

Table 1. Rearrangements of (**1**) and (**2**) with base.[a]

Compound	Base	Solvent	Time	Product	Yield (%)
(**1a**)	DBU	CH_2Cl_2	5 min	(**3a**)	83
(**1a**)	K_2CO_3	CH_2Cl_2	3·5 h	(**3a**)	85
(**1b**)	DBU	CH_2Cl_2	5 min	(**3b**)	85
(**1c**)	DBU	CH_2Cl_2	5 min	(**3a**)	56[b]
(**1c**)	K_2CO_3	CH_2Cl_2	5 h	(**3a**)	85
(**1d**)	K_2CO_3	CH_2Cl_2	5 h	(**3b**)	85
(**2a**)	DBU	$CHCl_3$	5 h	(**3a**)	15[c]
(**2b**)	DBU	$CHCl_3$	4·5 h	(**3b**)	16[c]
(**2c**)	DBU	$CHCl_3$	2 h	(**3a**)	86
(**2c**)	K_2CO_3	$CHCl_3$	6 h	(**3a**)	22[c]
(**2d**)	DBU	$CHCl_3$	2 h	(**3b**)	83
(**2e**)	DBU	$CHCl_3$	2 h	(**3c**)	80

[a] Carried out at room temperature using a slight excess of DBU or 2 mol. equiv. of potassium carbonate unless otherwise noted. [b] *S*-[(1,2-Benzisoxazol-3-yl)methyl]-*S*-phenylsulphoximide was also obtained in 22% yield. [c] Carried out under reflux. Recoveries of (**2a**), (**2b**), and (**2c**) were 65, 63, and 63%, respectively.



(**5**)

of (**5**) was also confirmed by elemental and spectral analyses, especially by the ^1H n.m.r. spectrum which showed the presence of the partial structure PhNHNHCHNH–: ν 3050 cm^{-1} (NH), 1025 and/or 1040 cm^{-1} (SO); δ (100 MHz; $CDCl_3$) 6.7—8.1 (m, 14H, ArH), 6.24 (s, 1H, PhN*H*), 5.92 (dd, *J* 8.1 and 9.7 Hz, 1H, NHC*H*NH), 5.56 (d, *J* 9.7 Hz, 1H, CHN*H*S), and 4.20 (d, *J* 8.1 Hz, 1H, NHN*H*CH); deuteriation with D_2O resulted in disappearance of the peaks at δ 6.24, 5.56, and 4.20 and in collapse of the dd peak at δ 5.92 into a singlet. These data support the sulphinylimine structure of compounds (**3**).

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2 T. Yoshida, S. Naruto, and H. Nishimura, *Tetrahedron Lett.*, 1980, **21**, 2315; T. Yoshida, S. Naruto, H. Uno, and H. Nishimura, *Chem. Pharm. Bull.*, accepted for publication.