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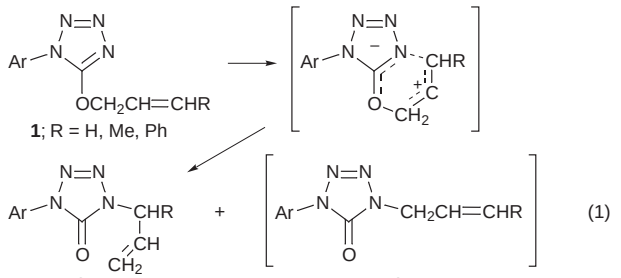
Thermal Rearrangement of 3-Allyloxy-1,2-benzisothiazole 1,1-Dioxides: an Unusual Inversion of Products of Sigmatropic [3,3]-Shift to Give the [1,3]-Isomers†

M. Lurdes S. Cristiano,*[a] Amadeu F. Brigas,[a] Robert A. W. Johnstone,[a,b] Rui M. S. Loureiro[a,b] and Paula C. A. Pena[a]

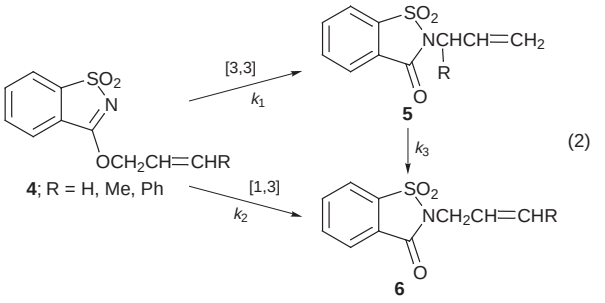
[a] *UCEH, Campus de Gambelas, Universidade do Algarve, 8000 Faro, Portugal*
[b] *Department of Chemistry, University of Liverpool, Liverpool L69 3BX, UK*

3-Allyloxy-1,2-benzisothiazole 1,1-dioxides **4** isomerize thermally to give [3,3]- and [1,3]-products **5**, **6** of sigmatropic shift, of which the former reacts further to give solely the [1,3]-isomer.

Previously, it has been shown that thermal isomerization of a range of 5-allyloxy-1-aryltetrazoles **1** proceeds *via* concerted sigmatropic [3,3]-inversion of allyl during its shift from *O* to *N* to give the tetrazolone product **2** [reaction (1)].[1] None of the tetrazolone product **3** from a [1,3]-shift was observed. Kinetic and cross-over experiments[1,2] indicated that the rearrangement was intramolecular and proceeded through a polar transition state, in which the heterocyclic part bears a partial negative charge and the migrating allyl a partial positive charge. No products of [1,3]-migration, indicative of an ionic mechamism,[3] were observed. Attempts to induce a [1,3]-shift at lower temperatures through an ionic mechanism through the use of lithium perchlorate[4] failed to produce any isomerization.[1,5]

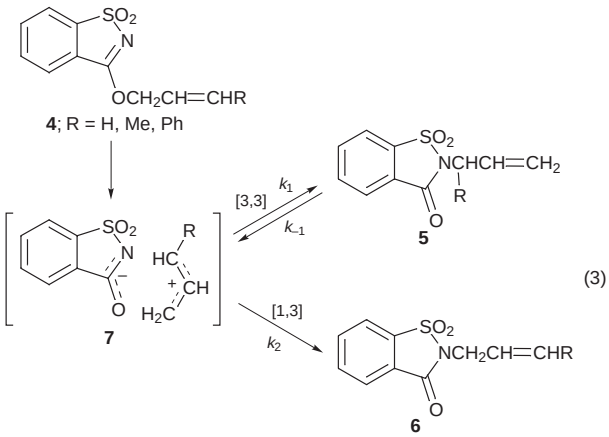


(1)



(2)

In complete contrast with these earlier results, a series of analogous 3-allyloxy-1,2-benzisothiazole 1,1-dioxides **4** [reaction (2)] formed products of both [3,3]- and [1,3]-rearrangement. In non-polar solvents such as toluene, the rearrangement proceeded slowly at 85 °C to give mostly the [3,3]-isomer **5** characteristic of a concerted sigmatropic shift of allyl from *O* to *N* (Table 1). Unlike the tetrazoles, some [1,3]-shifted product was observed. In polar media, such as ethanol or toluene–triethylamine, at similar temperatures, rearrangement was much faster and gave predominantly the [1,3]-isomer **6**, characteristic of an ionic intermediate or transition state (Table 1). Thus, for the strongly electron-withdrawing tetrazolyl heterocycle there is only one concerted polar intramolecular allylic shift but, for the almost equally strongly electron-withdrawing 'saccharyl' group,[6] there appear to be two mechanisms of migration, one concerted and the other possibly ionic.



(3)

The course of rearrangement (2) was monitored by ^{1}H NMR spectroscopy, which not only allowed the [3,3]- and [1,3]-products of migration to be distinguished easily and quantitatively measured but also showed there were substantially no other products of reaction. From such experiments and treating the kinetics as first-order, respective approximate rate constants of 0.8×10^{-5} s^{-1} (k_1) and 1.3×10^{-5} s^{-1} (k_2) were determined in toluene at 85 °C for the formation of the [1,3]- and [3,3]-isomers of the phenyl-substituted allylic derivative **4** (R = Ph). However, the ^{1}H NMR studies also revealed that, on extended heating of the mixture of [1,3]- and [3,3]-products **5**, **6** (R = Me, Ph) the ratios of their respective amounts changed in favour of the [1,3]-isomer. Since no other substances were formed, it could be concluded that there must have been a second rearrangement involving an allylic inversion from the [3,3]-product of a concerted shift **5** to give the product of a probable ionic [1,3]-shift **6** [reactions (2) and (3)]. On extended heating of the neat compound **4** (R = Ph) at 135 °C, eventually only the product **6** of [1,3] migration was present. A similar result was found for compound **4** (R = Me), except that longer heating was required at the same temperature. As for the rate constants (k_1, k_2), first order kinetics were assumed to extract an approximate rate

* To receive any correspondence (*e-mail*: mcristi@ualg.pt).
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Table 1 Ratios of products **5**, **6** from the rearrangement of 3-allyloxy-1,2-benzisothiazole 1,1-dioxides **4** (R = Me, Ph) in different solvents [reaction (2)]

4; R	Solvent	t/°C	t/h	% [3,3]-product **5**	% [1,3]-product **6**	% Unchanged starting material **4**[a]
Ph	Toluene	110	20	87	13	0
Ph	Toluene	85	20	10	2	88
Ph	Ethanol	78	4	46	54	0
Ph	Toluene–triethylamine	105	2.5	28	72	0
Ph	Neat liquid	160	4 (2)[b]	21 (46)[b]	79 (54)[b]	0
Me	Toluene	110	18	82	18	0
Me	Ethanol	78	3	27	2	71

[a]The time for complete disappearance of starting material is only approximate. [b]Values in parentheses indicate the observed percentages after 2 h, illustrating the changing ratio of [3,3]- and [1,3]-products on extended heating to 4 h.

Table 2 Calculated enthalpies of formation and activation for the rearrangement of 3-allyloxy-1,2-benzisothiazole 1,1-dioxide **4** (R = H) to give [3,3]-product **5** and [1,3]-product **6** in toluene and methanol by concerted and ionic mechanisms

R = H[a]	ΔH_f/kJ mol^{-1}	ΔH_R/kJ mol^{-1} **A** → **B**[b]	ΔH^*/kJ mol^{-1} concerted[c]	ΔH^*/kJ mol^{-1} ionic[d]
Ethanol				
4	−242	**4** → **5** or **6**	**4** → **5**	**4** → **7**
5	−259	−17	163	171
6	−259			**7** → **6**
7	−71			0
Toluene				
4	−188	**4** → **5** or **6**	**4** → **5**	**4** → **7**
5	−213	−25	167	259
6	−213			**7** → **6**
7	67			0

[a] For **4** (R = H), structure **5** is the same as structure **6**. [b]Enthalpy of reaction. [c]Enthalpy of activation for a concerted process [reaction (2)]. [d]Enthalpy of activation for an ionic process [reaction (3)].

constant (k_3) of 0.2×10^{-5} s^{-1} for the inversion of isomer **5** to **6** [reaction (2)], although this rate constant can also be interpreted as that for the reverse reaction [k_{-1}, reaction (3)]. This reversion of a concerted sigmatropic rearrangement to give the product of a similar ionic rearrangement appears to be highly unusual amongst the many known 'Claisen' type rearrangements.[7] The somewhat analogous 'Chapman' rearrangement of a benzyl group from *O* to *N* in 3-benzyloxy-1,2-benzisothiazole l,l-dioxides has been shown to proceed through an ionic mechanism.[8] The reaction is not similar to those that form abnormal products with allylic ethers of phenols.[9]

To examine the relative transition state activation energies in greater detail, calculations[10] were carried out on the rearrangement of compound **4** (R = H) through concerted and ionic mechanisms in either ethanol or toluene as solvent. The results of these calculations are shown in Table 2. The activation enthalpies for the concerted reactions (**4** → **5**) in ethanol or toluene are predicted to be similar. For direct scission to an ionized state **7**, the activation enthalpy (**4** → **7**) in toluene is very much greater than that in ethanol, which itself is almost the same as for the concerted processes (Table 2). There is almost no activation energy for the collapse of the ionized state **7** to the rearranged product **5** or **6**. Thus, the results indicate that, for the migration of allyl (**4**, R = H), either [3,3]- or [1,3]-rearrangement can be expected almost equally but very slowly. It can be expected that the 'ionic' process will become easier as substituents on the migrating allyl group stabilize a positive charge. The initial experimental results support this supposition because the rate of rearrangement with a phenyl substituent (**4**; R = Ph) is very much faster than with a methyl substituent (**4**; R = Me) than with hydrogen (**4**; R = H). Further calculations at the Gaussian B3LYP/6-31G* level and accurate kinetic measurements are being undertaken.

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