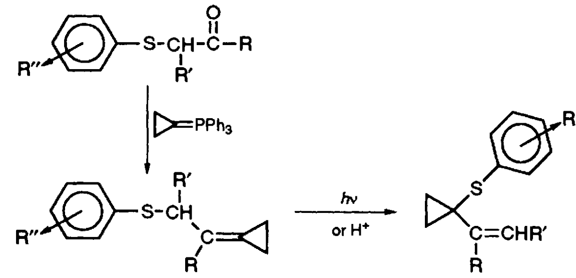
[1,3]-Shift of Arylthio Groups in 2-Cyclopropylidenealkyl-1-arylthio Derivatives

Angela M. Bernard and Pier P. Piras*

Dipartimento di Scienze Chimiche, Università di Cagliari, Via Ospedale 72, 09124 Cagliari, Italy

Light induced or acid catalysed [1,3]-arylthio shift in 2-cyclopropylidenealkyl-1-arylthio derivatives provides a convenient method for the synthesis of 1-arylthiovinyl cyclopropanes.

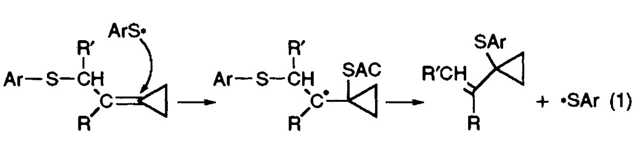
It is well known[1] that allyl sulfides can give thermal, photochemical or acid catalysed 1,3 phenylthio shift and that the rearrangement only takes place when it is 'down-hill' *i.e.* when the phenylthio group migrates from a secondary to a primary carbon or from a tertiary to either a secondary or a primary carbon. As far as we know there is only one example[2] of an 'up-hill' migration of a phenylthio group from a secondary origin to a tertiary terminus, by incorporating a trimethylsilyl group in the allyl sulfide. We here report that an 'up-hill' migration, probably assisted by strain energy relief, occurs from a primary or a secondary to a tertiary carbon in the cyclopropylidene derivatives **1a–d** leading to 1-arylthiovinylcyclopropanes[3] **2a–d** (Scheme 1). Compound **1** has been synthesised in good yields (60–82%) by the Wittig reaction of (3-bromopropyl)triphenylphosphonium bromide and the corresponding phenylthio ketone or aldehyde under McMurry's conditions.[4] Attempted purification of **1a–d**, by using a silica gel column led to variable ratio mixtures of **1** and **2**, whereas vacuum distillation led only to small amounts (2%) of **2**. Purification of **1a–d** was better carried out by column chromatography (basic alumina), this left only traces of **2a–d** (less than 5%).



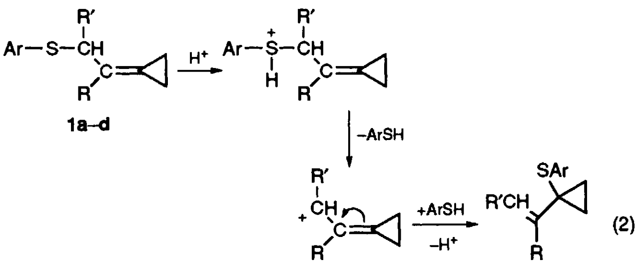
1a–d **2a–d**

a R = H, R' = Me, R'' = H
b R = Me, R' = H, R'' = H
c R = Me, R' = Me, R'' = H
d R = Me, R' = H, R'' = *p*-Me

Scheme 1



1a–d **2a–d**



1a–d **2a–d**

It was also found that isomerization can be carried out by exposing to day-light and, more rapidly and efficiently (yields >90%), by exposing $CDCl_3$ solution of **1a–d** to UV radiation (254 nm) normally used to inspect TLC plates.

These facts suggest that the isomerization can occur either through a light induced radical rearrangement or an acid catalysed [1,3] shift according to the experimental conditions. As a confirmation of the radical mechanism we found that the rearrangement can be prevented by wrapping the NMR tube with aluminium foil, but when two drops of thiophenol† were added to the chloroform solution of **1a–d**, even in a wrapped NMR tube, clean **1–2** rearrangement was recorded. The efficiency of the process may suggest a photochemically initiated radical reaction through an associative radical chain mechanism rather than a concerted process[1] [eqn. (1)]. Also, the fact that high yields of **2**‡ (75–95%) were obtained by reacting **1** with acetic acid at 80 °C for six hours in an aluminium wrapped flask, is a clear indication that the arylthio group migration can also take place in an acid catalysed reaction§ [eqn. (2)] by the other possible mechanism.

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Footnotes

† In the presence of oxygen aryl thiyl radicals are generated that can add to the double bonds.[5]

‡ The derivative **2a** was always obtained in the *E* configuration after UV or acidic treatment. (J_{H-H} = 15 Hz); isomerization of **1c** gave the *E* and *Z* isomers of **2c** in ratio 83:17. The configurations were attributed[6] on the basis of the $^3J_{C-H}$ of the methyl groups: *E* 7.92 Hz; *Z* 6.71 Hz.

§ At present, we cannot distinguish between a dissociative mechanism involving the intermediacy of an allyl cation and an associative mechanism involving a transition state with a negative charge localization on the sulfur and a corresponding positive charge at the β allyl centre.[7]

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