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Stereochemistry of the [4 + 2] cycloaddition reactions of 5-arylmethylene-2,4-dithioxo-1,3-thiazolidines with acrylonitrile, 1-ethoxy-3-phenyl-*E*-2-propen-1-one and 3-phenyl-*E*-2-propen-1-one

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The [4 + 2] cycloaddition reactions of 5-arylmethylene-2,4-dithioxo-1,3-thiazolidines with different dienophiles and separation of pure stereoisomeric products are reported.

Keywords: [4 + 2] cycloaddition reactions, 5-arylmethylene-2,4-dithioxo-1,3-thiazolidines

Acrylonitrile adds cyclically to the heterodiene component of *E,Z*-5-arylmethylene-2,4-dithioxo-1,3-thiazolidines **2a, b** in dioxane to afford mixtures of the two diastereomers of the cycloadducts **3** and **4**, from which pure **3a** and **3b** were obtained by chromatography and **4a** by fractional recrystallisation. Similarly, 1-ethoxy-3-phenyl-*E*-2-propen-1-one and 3-phenyl-*E*-2-propen-1-one react with **2a, b**, in dioxane-xylene (v/v 1:3) to furnish mixtures of **6** and **7**, in the former case, and **8** and **9**, in the latter one, from which pure **7a** only has been obtained by chromatography. However, fair yields of **6a** and **7b** have been obtained by performing the reactions in chloroform-ethyl acetate. The gross structures of the cycloadducts have been evidenced by IR, ^{1}H NMR (Table 3) and by mass spectral data (Table 2). Configurational assignments of compounds **6**–**9** are based exclusively on ^{1}H NMR spectroscopy. The extracted coupling constants inferred that H-5 and H-6 acquire the pseudoaxial positions in all diastereomers, whereas H-7 occupies the pseudoaxial orientation in compounds **6** and **8** and the pseudoequatorial position in compounds **7** and **9**. The energy optimised forms of compounds **6**–**9** calculated using the computer software molecular modelling program, show that isomers in which H-5, H-6 and H-7 acquire the pseudoaxial conformations must have the **5(*R*)**, **6(*S*)**, **7(*R*)** configuration (compounds **6** and **8**), whereas those compounds with a pseudoequatorial H-7 must have the **5(*R*)**, **6(*S*)**, **7(*R*)** configuration (compounds **7** and **9**). Moreover, the recorded $^3J_{6,7}$ of compounds **3** and **4** infer the pseudoaxial-pseudoequatorial relationship (Table 3). It is hard to believe that H-7 is the pseudoequatorial proton, as if so, the pseudoaxial H-6 must couple strongly with the neighboring pseudoaxial H-5, and this does not occur. Moreover, the recorded coupling constants of H-6 with the neighboring H-5 protons are not in accord with a pseudoequatorial H-6. These observations, beside others which deal with the coupling constants of H-2 and H-6 in the ^{1}H NMR spectra of 3-bromo-chromanone[22,23] and a thiopyrano[2,3-d]thiazole[6], respectively have prompted us to conclude that the hetero-ring is either distorted or labile. The easy conversion of **4b** into **3b** in boiling *n*-butanol is in accord with the labile nature of the ring.

Structures of all diastereomers are consistent with the regiochemical assignment, which is in accord with the favourable interaction between the sulphur atom of the heterodiene system and the β-carbon atom of the dienophile. Moreover, apart from **3** and **4**, which have labile rings, formation of all of the diastereomers with pseudoaxial H-5 and H-6 supports the hypothesis that the cycloaddition has occurred with retention of configuration of the dienophile. The formation of diastereomers having pseudoaxial H-7 (compounds **6** and **8**) and others having pseudoequatorial H-7 (compounds **7** and **9**) in ratios comparable to those of the *E,Z*-isomers of the starting dithioxo- compounds **2a, b** supports the high stereospecificity of the reaction.

Software used: 3D Molecular Modeling Software, Alchemy III, Tripos Associates, Inc, a subsidiary of Evans& Sutherland, 1992.

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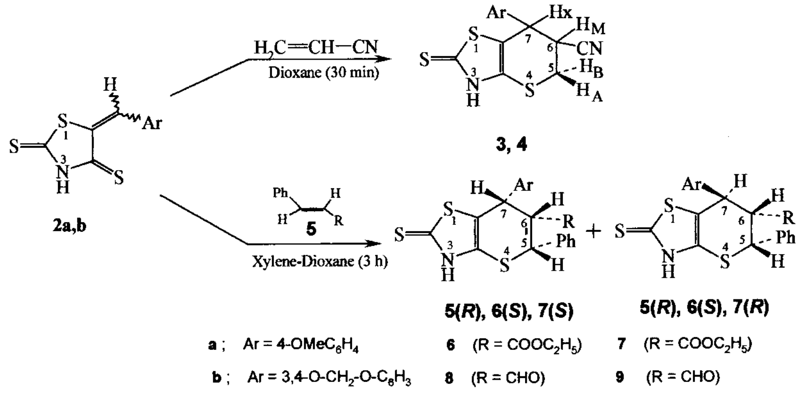

Scheme 1 Reactions of **2a,b** with acrylonitrile, 1-ethoxy-3-phenyl-*E*-2-propen-1-one and 3-phenyl-*E*-2-propen-1-one.

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