OXIDATION OF 4-ACETYL-2-METHYLTHIO-Δ^2-1,3,4-THIADIAZOLINES WITH m-CHLOROPERBENZOIC ACID AND REACTION OF THE OXIDATION PRODUCTS

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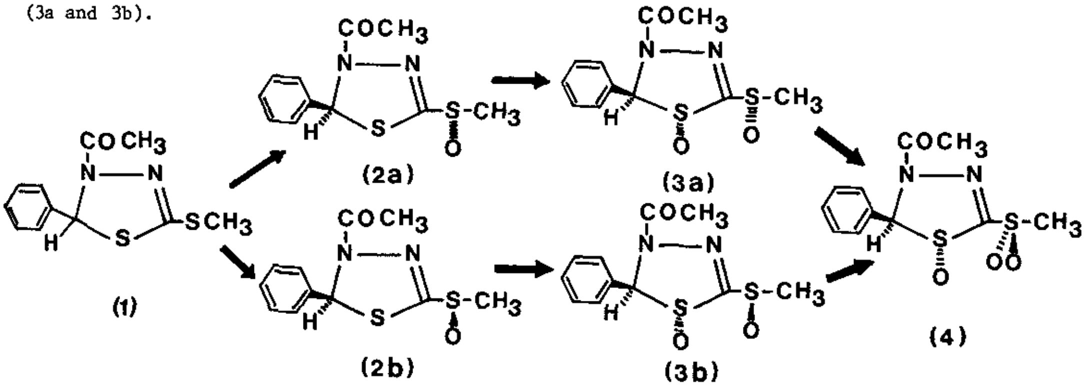
4-Acetyl-2-methylsulfonyl-5-phenyl-Δ^2-1,3,4-thiadiazoline 1-oxide (4) was obtained by oxidation of 4-acetyl-2-methylthio-5-phenyl-Δ^2-1,3,4-thiadiazoline (1) with m-chloroperbenzoic acid at room temperature. It was found that the oxidation of compound (1) to compound (4) proceeds by way of the diastereomeric mixture of 4-acetyl-2-methylsulfinyl-5-phenyl-Δ^2-1,3,4-thiadiazolines (2a and 2b) and 4-acetyl-2-methylsulfinyl-5-phenyl-Δ^2-1,3,4-thiadiazoline 1-oxides (3a and 3b).



The detailed structures of compounds 2a and 3b were established by single-crystal X-ray analysis. Treatment of compounds (3a and 3b) with triethylamine gave 2-methylsulfinyl-5-phenyl-1,3,4-thiadiazole. The methylsulfinyl group of compound (2) can be removed by treatment with sodium borohydride or sodium hydrosulfite, and replaced by various nucleophiles, including active methylene compounds (ethyl malonate, ethyl acetoacetate, ethyl cyanoacetate). Similarly, oxidation of different 5-substituted 4-acetyl-2-methylthio-Δ^2-1,3,4-thiadiazolines and the reaction of the oxidation products was also examined.