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Stereospecific thionation of 2-ethoxy-1-2-oxaphosphorinane 2-oxide and its derivatives with Lawesson's reagent

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Abstract

The parent phostone, 2-ethoxy-1,2-oxaphosphorinane 2-oxide 1, and derivatives with substituents at the 3-position (methyl, phenyl, and benzyl; compounds 2-4) were convened with Lawesson's reagent to provide the corresponding sulfide analogues 5-8 in moderate yields. The conversion of 2-4 occurred with retention of configuration at the phosphorus center. This was implied from the relative R(f) values and 13C and 31P NMR chemical shifts of the individual isomers and confirmed for the transformation of 3b to 7b by X-ray structures of each of these. Oxidation of 7b, 8a, and 8b with m-chloroperoxybenzoic acid alone led to the corresponding oxides 3b, 4a, and 4b with retention. The presence of trifluoroacetic acid during this oxidation process led to varying degrees of epimerization about phosphorus and was dependent on the relative molar equivalents of this acid.

Keywords

2-ethoxy-1,2-oxaphosphorinane 2-oxide, 2-ethoxy-1,2-oxaphosphorinane 2-sulfide, Lawesson's reagent, Phostone, Stereoselective synthesis, Thiophostone, X-ray diffraction