

SYNTHESIS OF METHYLENE-BRIDGED SATURATED 1,3-BENZOXAZINES

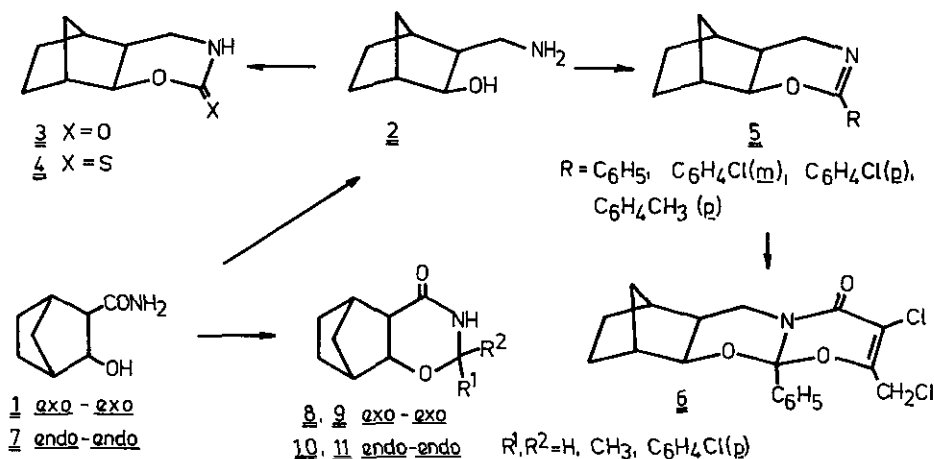
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In the present work we report the synthesis of isomers of tricyclic 1,3-oxazines and oxazinones prepared by us previously (G. Stájer, A. E. Szabó, F. Fülöp, G. Bernáth, P. Sohár, J. Heterocyclic Chem. submitted for publication). In contrast with the earlier-studied compounds, not the nitrogen atom but the oxygen atom of the hetero ring is attached to the carbobicyclic skeleton.

The 1,3-oxazin-2-one and 2-thione **3** and **4** prepared via the corresponding carbamate and dithiocarbamate from the aminoalcohol **2**, made by LiAlH_4 reduction of **1**. The latter resulted from the hydrolysis of a norbornene and trichloroacetyl isocyanate adduct. Compound **2** and imidates yielded **5**, from which azetidinones and **6** were made with chloroacetyl chloride. The latter reaction is regarded as a new preparation of 1,3-oxazines.



1 was oxidized to the 2-oxo derivative, then reduced with NaBH_4 to the diendo compound **7**. With acetone, **1** and **7** furnished **8** and **10**, and with p-chlorobenzaldehyde isomers **9** and **11**. A comparative ^1H - and ^{13}C -nmr study was carried out on the related fused-skeleton bicyclic heterocycles prepared earlier and the above compounds, having a flexible hetero ring attached to a rigid skeleton.