SYNTHESIS OF METHYLENE-BRIDGED SATURATED 1,3-BENZOXAZINES

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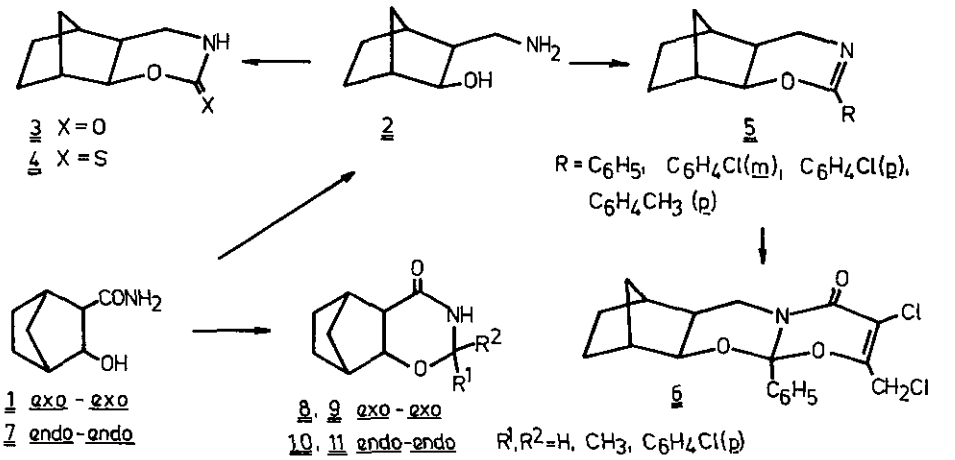
In the present work we report the synthesis of isomers of tricyclic 1,3--oxazines and oxazinones prepared by us previously (G. Stájer, A. E. Szabó, F. Fülöp, G. Bernáth, P. Sohár, J. Heterocyclic Chem. submitted for publication). In contrast with the earlier-studied compounds, not the nitrogen atom but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



3 X=O
4 X=S

2

5
R = C_6H_5, C_6H_4Cl(m), C_6H_4Cl(p), $C_6H_4CH_3$ (p)

1 exo-exo
7 endo-endo

8, **9** exo-exo
10, **11** endo-endo

6

R^1,R^2=H, CH_3, C_6H_4Cl(p)

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.