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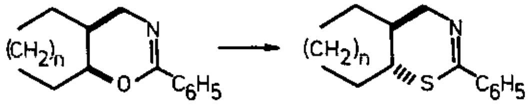
SYNTHESIS AND STEREOCHEMICAL STUDIES OF CIS AND TRANS CONDENSED-SKELETON 5,6-DIHYDRO-2-PHENYL-4H-1,3-THIAZINES. AN UNEXPECTED SPIROCYCLIZATION

Lajos Simon, Simonné G. Talpas, Ferenc Fülöp, Gábor Bernáth, Pál Sohár[x]

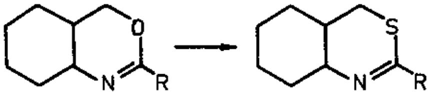
Institute of Pharmaceutical Chemistry, University Medical School Szeged, Hungary
[x]Spectroscopic Department of EGYT Pharmacochemical Works, Budapest, Hungary

We found that *cis*-5,6-alkylene-5,6-dihydro-2-phenyl-4H-1,3-oxazines (1) could be converted into the corresponding *trans*-1,3-thiazines (2) via a method (P_4S_{10}, 130 °C) analogous to that used by Meyers for related purposes (J. Org. Chem. 25, 1147 /1960/). In contrast, the corresponding *trans* isomers could not be transformed even when a longer reaction time and/or elevated temperature was applied, but most of the starting material was recovered unchanged. However, in the case of both the *cis* and *trans* positional isomers, the 3 → 4 O → S exchange could be carried out with good yields.



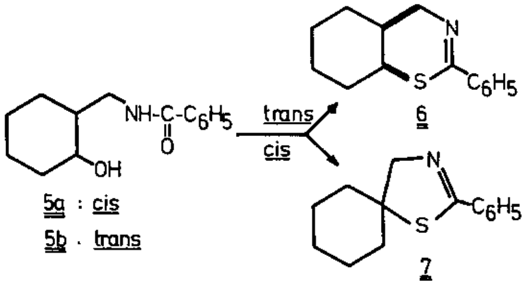
1 2

n = 1, 2, 3

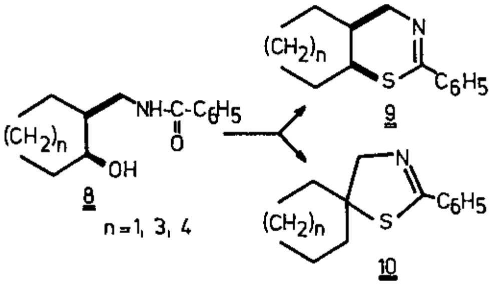


3 4

cis or *trans*; R = $C_6H_4Cl(p)$



5a : *cis*
5b : *trans*
6
7



8
n = 1, 3, 4
9
10

cis-5,6-Tetramethylene-5,6-dihydro-2-phenyl-4H-1,3-thiazine (6) was obtained by heating 5b with P_4S_{10}. In the analogous reaction with the *cis* isomer 5a, an unexpected spirocyclization was observed and 1-thia-2-phenyl-3-azaspiro(4,5)-decene-2 (7) was obtained. When *cis*-2-benzoylaminomethyl-1-cyclopentanol (8, n = 1) was heated with P_4S_{10}, thiazine 9 and spiro compound 10 were formed in 1:1 ratio, but in different ratios for the higher homologues (8, n = 3, 4). An X-ray diffraction study of *trans*-5,6-trimethylene-5,6-dihydro-2-phenyl-4H-1,3-thiazine (2, n = 1) showed that the C(5)-C(6) bond is significantly shortened, which explains the unusual formation of the *trans*-trimethylene derivative.