Aminolysis of $\alpha$-Santonin in the Reaction with Dimethylamine

Arman T. Kulyjasov, Nariman S. Tleugabulov, Koblandy M. Turdybekov, Sergazy M. Adekenov

*Institute of Phytochemistry MS-AS Republic of Kazakhstan, 470032 Karaganda, Erdzanova av., postbox 19. Fax: +7 (321 2) 51 1023. E-mail: arglabin@phyto.karaganda.su*

It is well known that opening of lactone cycle of 1 occurs at room temperature in benzene solution within 4 hours with high yield when $\alpha$-santonin (1) treated with pyrollidine. However, dimethylamine doesn’t cause the reaction in the same conditions even when mixture is boiled. We successfully conducted the reaction with NHMe$_2$ in boiling dioxane during 4.5 hours. Yield of product 2 is 42%. The structure of amide (2) has been established by X-ray data.

The bond lengths and bond angles of 2 are close to usual ones within the range of precision. Torsional angles C1C10C5C4 and C9C10C5C6 equal to 1.4° and 59.8° accordingly. Presence of double bonds C1=C2 and C4=C5 conjugated with keto-group C3=O1 leads to strong flattening of cycle A (absolute value of intracycle torsion angles doesn’t exceed 1.5°). The cycle atoms are coplanar within ±0.0064 A. Atom O1 is located on the cycle plane (torsion angle C1C2C3O1 is 177.3° and C5C4C3O1 is 177.2°). Cycle B takes the conformation of symmetric $7\alpha,10\beta$-chair ($C^7_5=0.7°$). Atoms 02 and C12 are equatorially oriented to $\alpha$- and $\beta$-side, correspondingly. In dimethylamine group we observed mesomer effect which was shown by reduction of bond length C12-N1 (1.334(3) A) and increase of bond C13=O3 (1.241(2) A) and also by flat trigonal coordination of nitrogen atom.