Summary

This work describes the synthesis of nonsymmetric ethylenediamine-substituted hexestrolderivatives and the investigation of the rearrangement of 2-(4-Hydroxyalkyl)-1,3-dioxolanes to 2-hydroxyethylalkanocesters.

In connection with the synthesis of these estrophilic ligands of the hexestrol series with cisplatin as the toxic principle, with a view to achieve a more selective treatment of uterus and breast cancers, the perchloric acid catalyzed hydrogenolysis of a 4:1 *syn/anti* mixture of epimeric 5-hydroxyacetals was studied. Surprisingly, instead of reductive removal of the benzylic hydroxygroup to afford the expected deoxygenated acetal, a diester was formed. Moreover, only a single isomer of this ester was diastereoselectively formed from the mixture of alcohols. The explanation for this apparent enigma turned out to be a redox reaction proceeding via cationic intermediates, which is observed here for the first time in an intramolecular reaction.

To investigate the mechanism of the new rearrangement a series of related 2-(4-hydroxyalkyl)-1,3-dioxolanes were synthesized and rearranged in the manner specified above. Finally, convincing evidence for hydrogen transfer from C1 to C5 was provided by the reaction of a deuterated 1,3-dioxolane derivative. This new reaction led to higher yields and a significant reduction of reaction steps towards the synthesis of new hexestrolderivatives.

To connect the complexing ethylenediamine-group to the hexestrolderivatives two separate strategies were used. The ester resulting from the rearrangement is transformed into the amine by heating in ethylenediamine followed by reduction with LAH and catalytic amount of $AlCl_3$.

Another way towards the amine uses the two step transformation of the ester to an iodide. Hydrophilic chains can be included into the molecule by substitution of the iodide with ethyleneglycolderivatives and iodination of the resulting hydroxygroup. The iodide is converted into the ethylenediaminegroup by dissolving in ethylenediamine and heating.

To set-up the cisplatin-group in the estrophilic ligand, the simplest representative was complexed with K_2PtCl_4.