

New data on the "*t*-Amino effect" in series of 4-R-N,N-dimethylanilines

O.N.Semenova, Ye.Ye.Artyukhova, I.G.Yermolenko, L.D.Patsenker

Institute for Single Crystals, National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

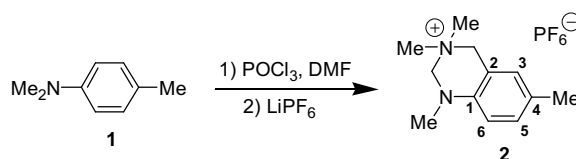
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The reaction of 4-R-N,N-dimethylanilines with POCl_3 and DMF is investigated. This reaction is of considerable interest as a way for synthesis of the organic luminophores, pharmaceutical substances, and intermediate products. Electron donor substituents were found to favour the formation of tetrahydro-quinazolinium salts while the presence of electron-withdrawing groups (e.g. cyano and carboxy groups) preferably led to the formation of formylated products. In the case of weak electronic influence ($\text{R} = \text{Me}$ and Br) a mixture of aldehyde and the cyclic salt is formed. Increased reaction times favour the formation of cyclic quaternary salts. The experimental results are discussed using quantum-chemical simulations.

Исследована реакция 4-R-N,N-диметиланилинов с POCl_3 и ДМФ. Эта реакция представляет интерес как метод синтеза органических люминофоров, биологически активных веществ и полупродуктов органического синтеза. Обнаружено, что электронодонорные заместители способствуют образованию тетрагидро-хиназолиниевых солей, в то время как в присутствии электроноакцепторных групп (таких как циано и карбокси групп), предпочтительно образуются формилированные продукты. В случае заместителей со слабым электронным влиянием ($\text{R} = \text{Me}$ и Br) образуется смесь альдегида и циклической соли. Увеличение продолжительности реакции способствует циклизации. Экспериментальные данные обсуждаются с использованием квантово-химических расчетов.

The Vilsmeier–Haack reaction based on the POCl_3 –DMF complex is a well-known method for the formylation of a wide range of π -electron-rich aromatic compounds. This method is widely used for synthesis and modification of organic compounds — potential luminophores, pharmaceutical substances, intermediate products, etc. However, the electrophilic reaction at the *ortho*-position to a tertiary amino group may favour the heterocyclization of the intermediate iminium salt to give tetrahydro-quinazolinium salt instead of the formylation reaction. A such reaction pathway was found previously for N,N-dimethyl-4-toluidine (**1**) which forms cyclic quaternary salt **2** (Scheme 1) [1, 2], for series of 4-dimethylamino naphthalic acid [3–5], 2,5-diaryl-1,3-oxazole, 2,5-diaryl-1,3,4-oxadiazole [6] de-

rivatives, and several other compounds. This type of cyclization reaction is known as the "*t*-amino effect" [7, 8]. Such reaction is of considerable theoretical interest as an example of the surprisingly running cyclizations and in addition it presents a convenient way for synthesis of water soluble organic compounds, particularly organic luminophores [3–6]. The mechanism for the heterocyclization reaction including the two-step cycloisomerisation of the interme-



Scheme 1.