3,4-Diacetylhexan-2,5-dion - an Effective Synthon for the Synthesis of Substituted Azulene Heteroanalogs by Cyclocondensation Reactions

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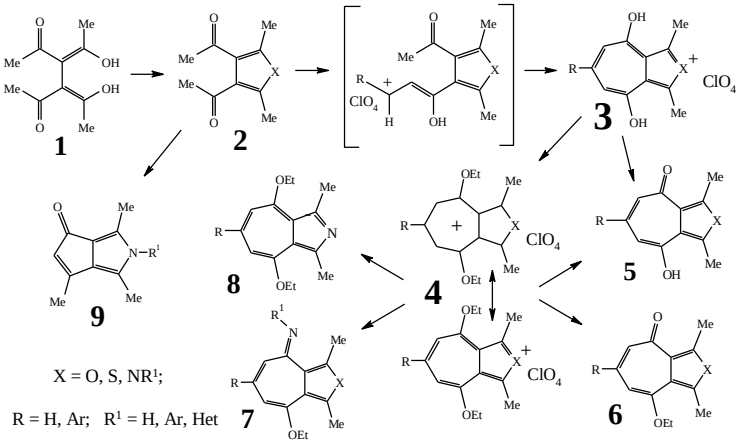
Universal, basically one-pot or, as a maximum, two-pot methods of synthesis of condensed tropone and tropolone derivatives - O-, S-, N- heteroanalogs of azulene were developed, as well as of the corresponding carbocations having an axial symmetry of structure [1, 2]. 3,4-Diacetylhexan-2,5-dion (tetraacetyletane) **1** existing in a form of di-ketoenol have been used as an initial basic synthon. Synthon **1** is simultaneously 1,3- and 1,4-diketone, so it forms five-membered heterocycles **2** (X = O, S, N-R^1) in a presence of acid; these possess acetyl groups in positions 3 and 4 which are convenient to complete a seven-membered ring.



So, oxygen analogs of azulene - perchlorates of **3** e **4** (O = I) - were obtained in high yield in an one-pot synthesis by means of acid-catalyzed ($HClO_4$) condensation of bis-ketoenol **1** with trialkylorthoformates and/or aromatic aldehydes in an acetic anhydride media. Optimum variants of N- and S-heteroazulenes **3** and **4** syntheses are analogous to above, but they include preliminary stage of diacetylpyrrol and -thiophene **2** (X = N-R^1, S) formation from **1**.

The distribution of electron deficit in azulenium cations **3, 4** distinctively depends on the character of heteroatom: if O = I than positive charge is de-localized predominantly within seven-membered ring; if O = N-R^1 than this is localized on the heteroatom, and if X = S than electronic distribution has an intermediate character. Reactivity of carbocations **3, 4** in hydrolysis and aminolysis processes leading to heteroannelated tropolones and troponimines **5-7** varies with respect to above mentioned electron deficit distribution. 1,3-Dimethyl-4,8-diethoxy-2-azaazulene **8** - direct azulene heteroanalog was obtained for the first time. It was found as well that diacetylpyrroles **2** (X = N-R^1) undergo intramolecular cyclocondensation into azapentalenones **9** on heating above 180^{i}N.

[1] E.P. Olekhnovich, S.L. Boroshko, G.S. Borodkin, I.V. Korobka, V.I. Minkin, L.P. Olekhnovich, *Zh. Org. Khim., 1997, **33**, 267 [Russ. J.Org.Chem., 1997, **33** (Engl.Transl.)]* .

[2] L.P. Olekhnovich, S.L. Boroshko, Yu.N. Tkachenko, A.F. Pozharskii, E.B. Tsupak, Yu.A. Zhdanov, L.P.Olekhnovich. *Izv. Akad. Nauk Ser. Khim., 1998,No. 8, 1596.*