Synthesis of Functionalized Anthraquinones from 1-Aryl-3-(trimethylsilyl)-oxy-1,3-butadienes and Derivatives of Quinopimaric Acid

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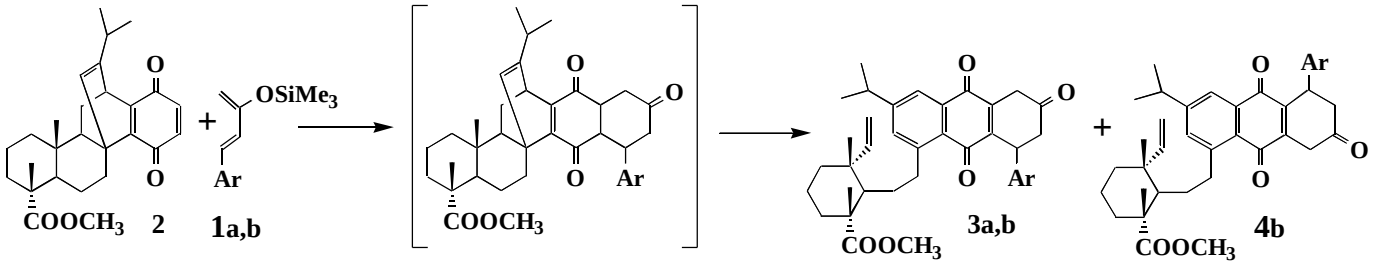
Previously we have developed an approach to the synthesis of quinones containing the aromatic[1] or terpenoid substituent[2]. These compounds and their natural analogues have high antitumour and antivirus activity, also effecting *SNC*. In the present communication the way to the synthesis of quinones, bearing both aromatic and terpenoid fragment is described.

The reaction between 1-aryl-3-(trimethylsilyl)-oxy-1,3-butadiene **1a** and methyl ester of quinopimaric acid **2** in boiling dioxane during 24 h leads regioselectively to a product **3a** with 36% yield. Apparently, in the reaction conditions the splitting of the intermediate Diels-Alder adduct proceeds. Reaction of compounds **2** and **1b** affords two regioisomers **3b, 4b** in the ratio 4:6, overall yield is 60%.



Ar = 2-furil (**a**), 2-$(CH_3O)C_6H_4$ (**b**).

The thermal reaction of the methyl ester of dihydroquinopimaric acid (Diels-Alder adduct of levopimaric acid and benzoquinone) with dienes **1a,b** in described conditions failed. When catalytic reaction with the Et_2AlCl carried out (ratio diene **1b** : catalyst - 1.1:1), a product of dehydrogenation (quinone **2**, 64%) and product of hydroalumination-carbalumination (15%) were isolated. Reaction with the catalyst $Eu(fod)_3$ (ratio diene **1b** : catalyst - 1 : 0.20) gave 20% of quinone **2** and 58% appropriative hydroquinone. The formation of cycloadduct in both cases is not observed.

Thus, we find a route to quinones of complex structure having both aromatic and terpenoid substituent. From these compounds a wide range of biological activity should be expected.

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[1]G.A. Tolstikov, E.E. Shults, G.M. Safarova, L.V. Spirikhin, A.A. Panasenko // Zh. Organ. Khimii, 1990, v.26, n.6, pp.1283-96.

[2]G.A. Tolstikov, E.E. Shults, T.S. Mykhametzyanova, I.P. Baikova, L.V. Spirikhin // Zh. Organ. Khimii, 1993, v.29, n.4, pp.698-716.