

LETTERS TO THE EDITOR

NEW CONDENSED SYSTEMS – SUBSTITUTED OCTAHYDRO- CHROMENO[2,3,4-*k,l*]XANTHYLIUM SALTS

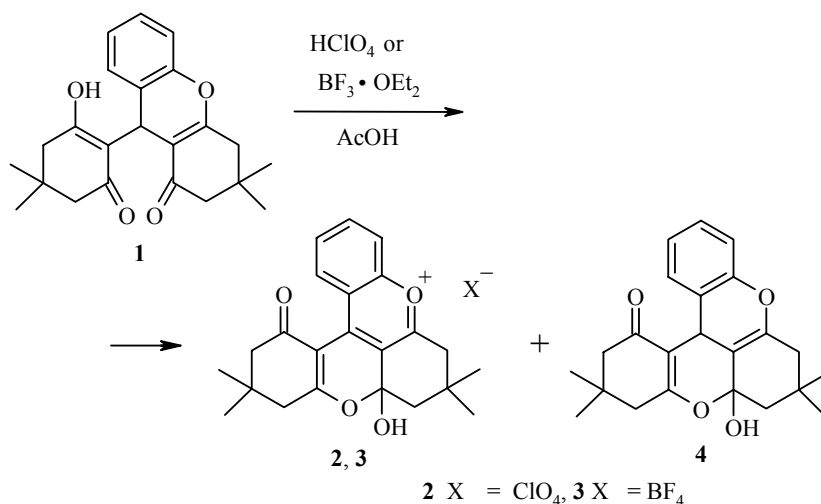
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Semicyclic 1,5-diketones of the 2-(3-oxopropyl)cyclohexane-1,3-dione series are capable of cyclization only in severe conditions on boiling in acetic anhydride to give substituted tetrahydrochromenones [1]. Salt formation is also difficult and takes place only with a donor substituent on C₍₁₎ of the aliphatic chain of the oxo compounds [2]. Reactions of analogous bicyclic oxo 1,5-diketones have not appeared in the periodic literature.

We have shown for the first time that it is possible to aromatize the tetrahydroxanthene ring of 3,3-dimethyl-9-(4,4-dimethyl-2,6-dioxocyclohexyl)-1,2,3,4-tetrahydro-9H-xanthen-1-one (**1**) under the influence of perchloric acid of boron trifluoride etherate with simultaneous polyacetalization of the 1,5-dicarbonyl unit into a hydroxytetrahydrochromen unit and formation of 8a-hydroxy-7,7,11,11-tetramethyl-13-oxo-6,7,8,8a,10,11,12,13-octahydrochromeno[2,3,4-*k,l*]xanthen-5-ylum perchlorate (**2**) or tetrafluoroborate (**3**) respectively. The yields of the salts were 42.2 and 57.5% respectively.

5a-Hydroxy-3,3,7,7-tetramethyl-1H-2,3,4,5a,6,7,8,13b-octahydrobenzopyrano[2,3,4-*k,l*]xanthen-1-one (**4**) was isolated along with salts **2** and **3** (12.2 and 21.0% yield respectively). The formation of **4** permits the suggestion that polyacetalization precedes aromatization of the heterocyclic fragment of the substrate.



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¹H NMR Spectra of DMSO-d₆ solutions with TMS as internal standard were recorded on a Bruker MSL-400 (400 MHz) instrument at 25°C.

Salts 2 and 3 and xanthenone 4. Perchloric acid (70%, 1.2 ml) was added over 1 h with constant stirring to a solution of compound **1** (2 g, 5.5 mmol) in a mixture of acetic acid (20 ml) and acetic anhydride (5 ml). The mixture was boiled for 6h. The solution was neutralized with Na₂CO₃, the solvent was partially evaporated and poured into diisopropyl ether (100 ml). The crystals formed were filtered off, washed with ether and dried to give the perchlorate **2**, in a yield of 1.07 g (42.2 %); mp 83-84°C. ¹H NMR spectrum, δ, ppm: 6.89-7.51 (4H, m, H_{arom}); 3.77 (1H, s, OH); 2.15-2.81 (8H, m, CH₂); 1.04-1.1 (12H, m, CH₃). Found, %: C 59.24; H 5.74; Cl 7.07. C₂₃H₂₅ClO₈. Calculated, %: C 59.42; H 5.42; Cl 7.63. The mother liquor was extracted with chloroform, the extract evaporated and dried to give hydroxybenzopyrano[2,3,4-*k,l*]xanthenone **4** (0.24 g, 12.2%); mp 192-194°C. ¹H NMR spectrum, δ, ppm: 6.92-7.10 (4H, m, H_{arom}); 5.18 (1H, s, H-13b); 3.72 (1H, s, OH); 2.07-2.44 (8H, m, CH₂); 0.99-1.08 (12H, m, CH₃). Found, %: C 74.92; H 7.23. C₂₃H₂₆O₄. Calculated, %: C 75.38; H 7.46.

8a-Hydroxy-7,7,11,11-tetramethyl-13-oxo-6,7,8,8a,10,11,12,13-octahydrochromeno[2,3,4-*k,l*]xanth-5-ylum tetrafluoroborate (3) was made analogously from the triketone **1** (1 g, 2.7 mmol) with a yield of 0.71 g (57.5%); mp 220-222°C. ¹H NMR spectrum, δ, ppm: 6.90-7.48 (4H, m, H_{arom}); 3.92 (1H, s, OH); 2.16-2.48 (8H, m, CH₂); 1.00-1.14 (12H, m, CH₃). Compound **4** was isolated in a quantity of 0.21 g (21%). Found, %: C 60.74; H 5.66. C₂₃H₂₅BF₄O₄. Calculated, %: C 61.08; H 5.57.

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