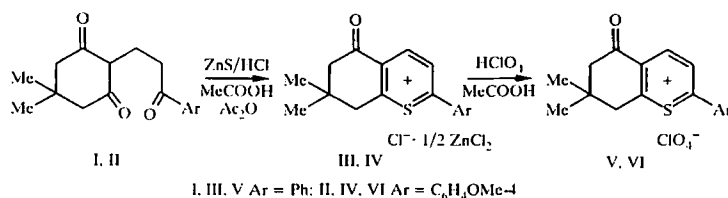


## LETTERS TO THE EDITOR

### SYNTHESIS OF 2-ARYL-5-OXOTETRAHYDRO- THIOCHROMENYLUM SALTS

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Semicyclic oxo-1,5-diketones of the 2-(3-oxopropyl)cyclohexane-1,3-dione series are less inclined to form salts than the usual 1,5-diketones. Thus, oxo-1,5-diketones containing phenyl groups at positions 1 and 3 of the side chain form only 5-oxotetrahydrothiochromenes under the action of sulfide reagents and acids [1]. The formation of thiochromenylium salts becomes possible only in the presence of electron-donating substituents in the phenyl rings [2].



We have established for the first time that oxo-1,5-diketones I,II containing no substituents at position 1 of the side chain can form salts. The action of zinc sulfide in acidic medium on compounds I and II leads to the corresponding chlorozincates III,IV in quantitative yield. In the exchange reaction with perchloric acid the compounds III,IV are converted into 5-oxotetrahydrothiochromenylium perchlorates V,VI.

In view of the high yields of salts III,IV it may be assumed that zinc chloride formed in the reaction medium leads to a stable anion but also catalyzes the heterocyclization process.

Acetic anhydride was added dropwise to mixture of concentrated hydrochloric acid (10 ml) and diethyl ether (15-20 ml) in an amount necessary to bind all the water. The initial diketone I,II (0.01 mol) and zinc sulfide (0.012 mol) were added to the solution obtained. After 12 h the precipitate of salts III,IV was separated and washed with ether.

Perchlorates V,VI were obtained by heating the salts III,IV in an excess of 57% HClO<sub>4</sub> on a water bath.

### EXPERIMENTAL

**7,7-Dimethyl-5-oxo-2-phenyl-5,6,7,8-tetrahydrothiochromenylium Chlorozincate (III).** Yield 73%; mp 192-194°C (acetic acid). Found, %: C 54.48; H 4.20; Cl 18.57; S 9.00. C<sub>17</sub>H<sub>17</sub>ClOS·0.5ZnCl<sub>2</sub>. Calculated, %: C 54.77; H 4.56; Cl 19.06; S 8.59. IR spectrum: 1708 (C=O), 1566, 1468, 1392 cm<sup>-1</sup> (tetrahydrothiochromenylium cation).

**7,7-Dimethyl-2-(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydrothiochromenylium Chlorozincate (IV).** Yield 76%; mp 220-222°C (acetic acid). Found, %: C 53.90; H 4.99; Cl 16.94; S 7.53. C<sub>18</sub>H<sub>19</sub>ClO<sub>2</sub>S·0.5ZnCl<sub>2</sub>. Calculated, %: C 53.66; H 4.72; Cl 17.64; S 7.95. IR spectrum: 1700 (C=O), 1596, 1562, 1472, 1340 cm<sup>-1</sup> (tetrahydrothiochromenylium cation).

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**7,7-Dimethyl-5-oxo-2-phenyl-5,6,7,8-tetrahydrothiochromenylium Perchlorate (V).** Yield 87%; mp 218-219°C (acetic acid). Found, %: C 55.19; H 4.42; Cl 9.21; S 8.42.  $C_{17}H_{17}ClO_5S$ . Calculated, %: C 55.36; H 4.61; Cl 9.63; S 8.68. IR spectrum: 1706 (C=O), 1560, 1468, 1394 (tetrahydrothiochromenylium cation), 1084  $cm^{-1}$  ( $ClO_4^-$ ).

**7,7-Dimethyl-2-(4-methoxyphenyl)-5-oxo-5,6,7,8-tetrahydrothiochromenylium Perchlorate (VI).** Yield 93%; mp 175-177°C (acetic acid). Found, %: C 53.91; H 5.27; Cl 8.42; S 7.71.  $C_{18}H_{19}ClO_6S$ . Calculated, %: C 54.20; H 4.77; Cl 8.91; S 8.03. IR spectrum: 1708 (C=O); 1562, 1472; 1392 (tetrahydrothiochromenylium cation); 1098  $cm^{-1}$  ( $ClO_4^-$ ).

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