

## 4-MERCAPTO-5,5-DIMETHYL-2-PHENYL- 2,3,5,6-TETRAHYDRO-7H-THIOCHROMEN- 7-YLIDENEMORPHOLINIUM PERCHLORATE

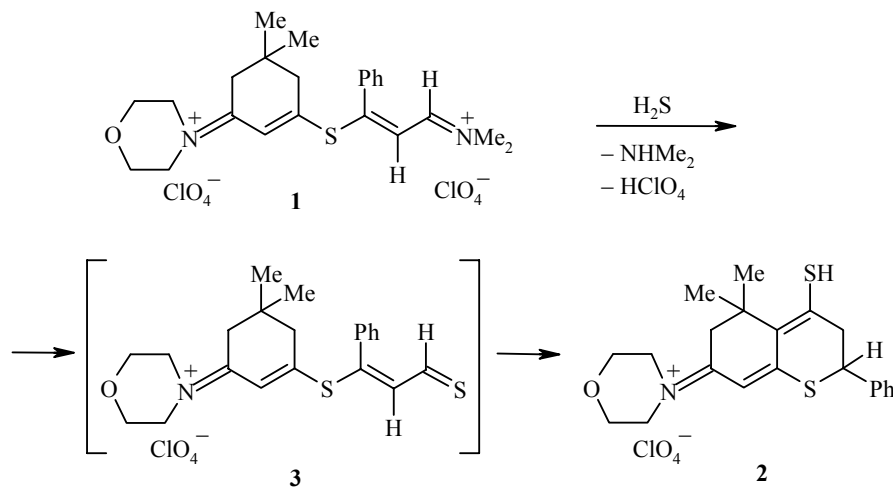
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**Keywords:** (1-N,N-dimethylimmonio-3-phenylprop-2-en-3-yl) (5,5-dimethyl-1-morpholinocyclohex-2-en-3-yl) sulfide diperchlorate, 4-mercapto-5,5-dimethyl-2-phenyl-2,3,5,6-tetrahydro-7H-thiochromen-7-ylidenemorpholinium perchlorate, hydrothiolysis.

We showed earlier that (1-N,N-dimethylimmonio-3-phenylprop-2-en-3-yl) (5,5-dimethyl-1-morpholinocyclohex-2-en-3-yl) sulfide diperchlorate (**1**) in methanol medium in the presence of a catalytic amount of triethylamine is readily converted to 5,5-dimethyl-7-morpholinio-2-phenyl-5,6-dihydro-7H-thiochromene perchlorate [**1**].

While studying hydrothiolysis of diperchlorate **1**, we found that the end product of its reaction with hydrogen sulfide in DMF is the previously unknown 4-mercapto-5,5-dimethyl-2-phenyl-2,3,5,6-tetrahydro-7H-thiochromen-7-ylidenemorpholinium perchlorate (**2**). The process probably occurs *via* intermediate formation of (3-phenyl-1-thioxoprop-2-en-3-yl) (5,5-dimethyl-1-morpholinocyclohex-2-en-3-yl) sulfide (**3**), which then undergoes ring closure.

This reaction is a novel example of synthesis of difficultly accessible thiochromene derivatives starting from enamino thioketones and halosubstituted immonium salts [**2**].



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**4-Mercapto-5,5-dimethyl-2-phenyl-2,3,5,6-tetrahydro-7H-thiochromen-7-ylidenemorpholinium Perchlorate (2).** Dry hydrogen sulfide was passed through a solution of (1-N,N-dimethylimmonio-3-phenylprop-2-en-3-yl) (5,5-dimethyl-1-morpholinocyclohex-2-en-3-yl) sulfide diperchlorate (**1**) (0.24 g, 0.4 mmol) [2] in DMF (5 ml) at 20°C for 30 min (TLC monitoring, Silufol, chloroform–ethyl acetate, 3:1). The reaction mixture was poured into ice–water mixture (30 g). The precipitate was filtered out, washed with water, and dried under vacuum over CaCl<sub>2</sub>. Obtained 0.15 g (80%) of compound **2** as a mustard color powder with mp 123-125°C. <sup>1</sup>H NMR spectrum (400 MHz, DMSO-d<sub>6</sub>, HMDS), δ, ppm: 0.82 and 0.87 (6H, s, 2CH<sub>3</sub>); 2.44 (2H, m, 6-CH<sub>2</sub>); 2.64 (2H, m, 3-CH<sub>2</sub>); 3.55 (1H, s, SH); 3.66 (1H, m, 2-CH); 3.67 and 3.83 (8H, m, CH<sub>2</sub>N+CH<sub>2</sub> and CH<sub>2</sub>OCH<sub>2</sub>); 6.30 (1H, s, HC=); 7.35-7.57 (5H, m, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR spectrum (DMSO-d<sub>6</sub>, HMDS), δ, ppm: 27.4, 27.6 (CH<sub>3</sub>); 34.5 (C<sub>(5)</sub>); 43.0 (=N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>); 50.3 (C<sub>(6)</sub>); 50.9 (C<sub>(3)</sub>); 63.4 (O(CH<sub>2</sub>)<sub>2</sub>); 66.1 (C<sub>(2)</sub>); 110.0 (C=N<sup>+</sup>); 122.1 (=C–H); 127-140 (CPh, C<sub>(4)</sub>, C<sub>(9)</sub>, C<sub>(10)</sub>). IR spectrum (KBr), ν, cm<sup>-1</sup>: 623 and 1096 (ClO<sub>4</sub>), 1556, 1576 (C=C), 1651 (C=N<sup>+</sup>), 2484 (SH). Found, %: C 54.20; H 5.45; Cl 6.84; N 2.17; S 13.82. C<sub>21</sub>H<sub>26</sub>ClNO<sub>5</sub>S<sub>2</sub>. Calculated, %: C 53.45; H 5.51; Cl 7.53; N 2.97; S 13.57.

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## REFERENCES

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