Chemistry of Heterocyclic Compounds, Vol.35, No. 6, 1999

LETTERS TO THE EDITOR

UNUSUAL CONVERSION OF SUBSTITUTED 5-OXO-5,6,7,8-TETRAHYDRO-4H-THIOCHROMENES WITH PHOSPHORUS PENTACHLORIDE

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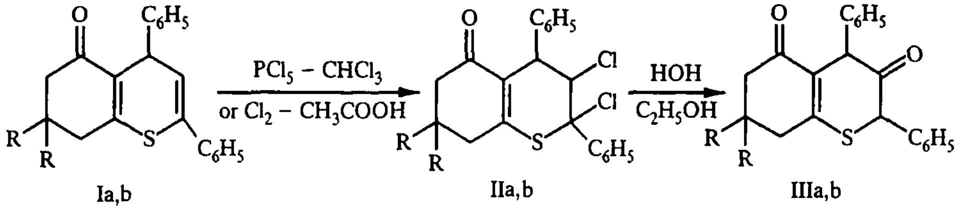
Nucleophilic substitution products – the corresponding gem-dihalogeno derivatives – are formed by reaction of carbonyl compounds with phosphorus pentachloride [1]. Several examples of the electrophilic addition of chlorine at the double bond by the action of phosphorus pentachloride are described in the literature [2].

In studying the reaction of phosphorus pentachloride with the substituted 5-oxo-5,6,7,8-tetrahydro-4H-thiochromenes Ia,b using the 1.3:1 reagent ratio, we found that interaction with the carbonyl group is not observed in chloroform at room temperature by maintaining the reaction mixture for 10 h. The products of the addition of chlorine to the double bond – the 2,3-dichloro-5-oxo-3,4,5,6,7,8-hexahydro-2H-thiochromenes IIa,b, which are identical to the compounds obtained by chlorination of the oxothiochromenes Ia,b in acetic acid, are formed.



a R = H, b R = CH_3

The compounds IIa,b are readily hydrolyzed by the heating in aqueous ethanol to form the corresponding 3,5-dioxo-3,4,5,6,7,8-hexahydro-2H-thiochromenes IIIa,b. The reaction of the oxo compounds Ia,b at the keto group with phosphorus pentachloride is probably impossible not only due to electronic, but also due to steric factors.

The reaction of the oxohydrothiochromenes Ia,b with chlorine and phosphorus pentachloride was accomplished by generally accepted methods [3, 4].

2,3-Dichloro-5-oxo-2,4-diphenyl-3,4,5,6,7,8-hexahydro-2H-thiochromene (IIa). Yield 80%; mp 154-155°C (ethanol). IR spectrum (vaseline oil): 1680 (C=O), 1645 cm^{-1} (C=C). PMR spectrum ($CDCl_3$): 2.25 (6H, m, 6-CH_2, 7-CH_2, 8-CH_2); 4.43 (1H, dd, $^3J = 9.5$ Hz, $^5J = 1.7$ Hz, 4-H); 4.83 (1H, d, $^3J = 9.5$ Hz, 3-H); 7.29 (8H, m, H_{arom}); 7.69 ppm (2H, m, H_{arom}). Found, %: C 64.44; H 4.87; Cl 18.17; S 8.20. $C_{21}H_{18}Cl_2OS$. Calculated, %: C 64.78; H 4.63; Cl 18.25; S 8.23.

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2,3-Dichloro-7,7-dimethyl-5-oxo-2,4-diphenyl-3,4,5,6,7,8-hexahydro-2H-thiochromene (IIb). Yield 76%; mp 159-160°C (ethanol). IR spectrum (mineral oil): 1685 (C=O), 1645 cm^{-1} (C=C). PMR spectrum ($CDCl_3$): 1.06 (3H, s, 7-Me); 1.08 (3H, s, 7-Me); 7.22 (2H, s, 8-CH_2); 2.42 (2H, d, ^5J = 1.7 Hz, 6-CH_2); 4.40 (1H, dd, ^3J = 9.4 Hz, ^5J = 1.7 Hz, 4-H); 4.86 (1H, d, ^3J = 9.4 Hz, 3-H); 7.29 (8H, m, H_{arom}); 7.69 ppm (2H, m, H_{arom}). Found, %: C 66.57; H 5.26; Cl 17.55; S 7.38. $C_{23}H_{22}Cl_2OS$. Calculated, %: C 66.18; H 5.27; Cl 17.02; S 7.67.

3,5-Dioxo-2,4-diphenyl-3,4,5,6,7,8-hexahydro-2H-thiochromene (IIIa). Yield 92%; mp 146-147°C (ethanol). IR spectrum (mineral oil): 1710, 1675 (C=O), 1654 cm^{-1} (C=C). PMR spectrum ($CDCl_3$): 2.45 (6H, m, 6-CH_2, 7-CH_2, 8-CH_2); 4.91 (1H, d, ^4J = 2.7 Hz, 2-H); 5.22 (1H, d, ^4J = 2.6 Hz, 4-H); 7.40 (6H, m, H_{arom}); 7.52 (2H, m, H_{arom}); 7.86 ppm (2H, m, H_{arom}). Found, %: C 75.60; H 5.46; S 9.47. $C_{21}H_{18}O_2S$. Calculated, %: C 75.45; H 5.39; S 9.58.

7,7-Dimethyl-3,5-dioxo-2,4-diphenyl-3,4,5,6,7,8-hexahydro-2H-thiochromene (IIIb). Yield 94%; mp 125-126°C (ethanol). IR spectrum (mineral oil): 1705, 1665 (C=O), 1640 cm^{-1} (C=C). PMR spectrum ($CDCl_3$): 1.09 (6H, s, two 7-Me); 2.21 (2H, s, 8-CH_2); 2.45 (2H, d, ^5J = 1.4 Hz, 6-CH_2); 4.93 (1H, d, ^4J = 2.7 Hz, 2-H); 5.19 (1H, d, ^4J = 2.6 Hz, 4-H); 7.32 (6H, m, H_{arom}); 7.52 (2H, m, H_{arom}); 7.86 ppm (2H, m, H_{arom}). Found, %: C 76.03; H 6.31; S 8.53. $C_{23}H_{22}O_2S$. Calculated, %: C 76.24; H 6.07; S 8.84.

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