10. A. A. Ishchenko, N. A. Derevyanko, M. A. Kudinova, G. G. Dyadyusha, and A. I. Tolmachev, Teor. Éksp. Khim., 13, 828 (1977).
11. G. G. Dyadyusha, I. V. Repyakh, and A. D. Kachkovskii, Teor. Éksp. Khim., 20, 398 (1984)
12. G. G. Dyadyusha, I. V. Repyakh, and A. D. Kachkovskii, Teor. Éksp. Khim., 21, 138 (1985)
13. N. A. Derevyanko, G. G. Dyadyusha, A. A. Ishchenko, and A. I. Tolmachev, Teor. Éksp. Khim., 19, 169 (1983).
14. A. A. Ishchenko, N. A. Derevyanko, V. M. Zubarovskii, and A. I. Tolmachev, Teor. Éksp. Khim., 20, 443 (1984).
15. A. I. Tolmachev, N. A. Derevyanko, and A. A. Ishchenko, Khim. Geterotsikl. Soedin., No. 9, 1178 (1982).

# SYNTHESIS AND RECYCLIZATION OF 4-CHLOROMETHYLFLAVYLIUM AND 4-CHLOROMETHYLBENZOTHIAPYRILIUM SALTS

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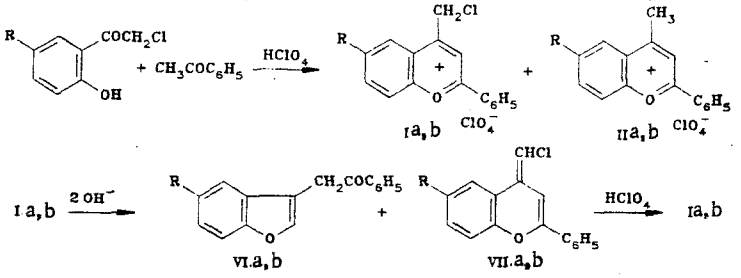
Condensation of α-chloro-o-hydroxyacetophenones in the presence of perchloric acid yields 4-chloromethylflavylium perchlorates. 4-Chloromethylbenzothiapyrilium perchlorates were obtained by intramolecular cyclization of 2-arylmercapto-5-chloropentanones-4. In the reaction of 4-chloromethylflavylium salts with aqueous alkali, chloromethyleneflavenes (the anhydro bases of the starting salts) and 3-phenacylbenzo[b]furanes were separated.

A feature of pyrilium salts is their ability to undergo ring contraction by the action of inorganic nucleophiles. Thus 2,3,4,6-tetraphenylpyrilium perbromide is converted by alkali to 2-benzoyl-3,4,5-triphenylfurane [1]. Later Balaban and Nenitzescu observed recyclization of trialkyl-substituted pyrilium salts to furanes by means of hydrogen peroxide [2]. Analogous ring contraction takes place during the oxidation of thiapyrilium cation and 1-benzothiapyrilium salts by manganese dioxide [3, 4]. Pyrilium ring contraction by recyclization of 4-chloromethylpyrilium salts to furylketones (the starting compounds for furopyrilium cation synthesis) in alkaline medium was recently reported [5]. The extension of this method to 4-chloromethylflavilium and 4-chloromethylbenzothiapyrilium salts would permit synthesis of the respective ketones of the benzo[b]furane and benzo[b]thiophene series.

The 4-chloromethylflavylium and 4-chloromethyl-1-benzothiapyrilium perchlorates have not been described. We find that the former can be obtained by the method used for the synthesis of 4-methylflavylium salts [6]. Indeed, condensation of α-chloro-o-hydroxyacetophenone with acetophenone in glacial acetic acid in the presence of perchloric acid gives 4-chloromethylflavylium perchlorates Ia,b. According to the PMR spectra, the respective 4-methylflavylium salts IIa,b form as byproducts, due to heterocyclic scission of the C–Cl bond in salts Ia,b. The amount of IIa,b depends on the duration of the reaction and is no more than 5% (the ratio is determined from the integrated intensities of the $CH_3$ and $CH_2$ signals).



I, II, VI, VII a R=H, b R=$CH_3$

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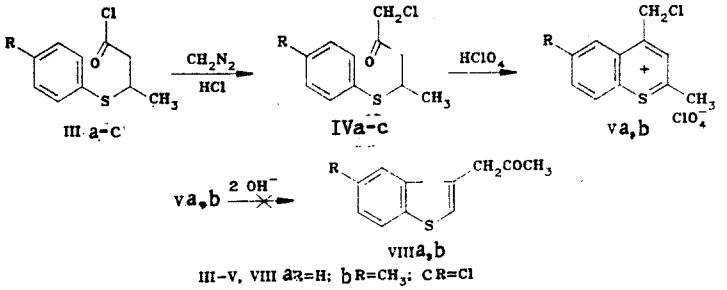
The PMR spectrum of salts Ia contains a methylene proton signal at 5.3 and aromatic proton signals in the 7.82-8.82 ppm region, while that of perchlorate Ib has an additional signal at 2.73 ppm for the methyl at position 6.

The starting compounds for the synthesis of the 4-chloromethylbenzothiapyrilium salts Va,b were 2-arylmercapto-5-chloropentanones-4 IVa-c; these were obtained from the respective β-arylmercaptobutyric acid chlorides IIIa-c and diazomethane and treatment of the intermediate diazoketones with hydrochloric acid. Cyclization of ketones IVa,b according to [7] with excess hydrochloric acid in the presence of triphenylmethyl chloride gives the 4-chloromethylbenzothiapyrilium salts Va,b. The attempt to cyclize ketone IVc to the corresponding salts was unsuccessful, probably because of the deactivating effect of the chlorine atom.




IIIa-c IVa-c Va,b VIIIa,b

III-V, VIII a R=H; b R=CH3; c R=Cl

The perchlorates Ia,b and Va,b have three reactive centers that can undergo nucleophilic attack, viz., the carbons at positions 2 and 4 of the pyrilium (or thiapyrilium) ring and the chloromethyl chlorine, if the reaction proceeds by a halophilic mechanism [8, 9]. We presume that attack by a strong nucleophile (aqueous alkali) can cause the pyrilium ring in salts I and V to open, with subsequent cyclization to form 3-phenacylbenzo[b]furanes VIa,b and 3-acetonylbenzo[b]thiophenes VIIIa,b. We established that when 4-chloromethylflavylium perchlorate Ia,b react with aqueous alkali in DMFA medium there are formed, besides the expected 3-phencaylbenzo[b]furanes VIa,b, the chloromethyleneflavenes VIIa,b (which are anhydrobases of salts Ia,b) and also unidentified polycondensation products.

In the presence of perchloric acid chloromethyleneflavenes VIIz, b are quantitatively converted to the starting perchlorates Ia,b. Recyclization of 4-chloromethyl-1-benzothiapyrilium perchlorates Va,b proceeds with much resinification so that individual compounds could not be isolated. The formation of polycondensation products is probably related to the tendency of the anhydrobases of salts Ia,b to undergo autocondensation [10].

## EXPERIMENTAL

IR spectra were obtained with a UR-20 instrument in mineral oil. PMR spectra were obtained with a Tesla BS-467 instrument (60 MHz), with TMS internal standard.

4-Chloromethylflavylium Perchlorate (Ia). A solution of 17.1 (0.1 mole) of α-chloro-o-hydroxyacetophenone, 12 g (0.1 mole) of acetophenone, and 14 ml (0.15 mole) of 70% perchloric acid in 80 ml of acetic acid was boiled for 5 h. The solution was cooled and 50 ml of ether was added. The crystalline precipitate was filtered off. Yield of Ia, 12.1 g (32%). $T_{dec}$ 260° (from acetic acid). Found, %: C 54.6, H 3.6, Cl 19.3. $C_{18}H_{12}Cl_2O_5$. Calculated, %: C 54.1, H 3.4, Cl 20.0.

4-Chloromethyl-6-methylflavylium Perchlorate (Ib). This was synthesized similarly. Yield 63%. $T_{dec}$ 270° (from acetic acid). IR spectrum: 1630, 1595, 1550, 1300, 1270, 1215, 1200, 1140, 1095, 930, 895, 830, 790 $cm^{-1}$. Found, %: C 56.0, H 3.4, Cl 18.0. $C_{17}H_{14}Cl_2O_5$. Calculated, %: C 55.3, H 3.8, Cl 19.0.

β-(Phenylmercapto)butyric (IIIa), β-(p-Tolylmercapto)butyric (IIIb), and β-(p-Chlorophenylmercapto)butyric Acid Chlorides (IIIc). These were synthesized by the method of [11].

2-Phenylmercapto-5-chloropentanone-4 (IVa). To a diazomethane solution prepared from 32 g (0.31 mole) of N-nitrosomethylurea in 300 ml of ether was added dropwise a solution of 21.3 g (0.1 mole) of β-(phenylmercapto)butyric acid chloride in 50 ml of dry ether. The solution was stirred for 3 h and let stand overnight. Then 100 ml of 35% hydrochloric acid was added with stirring and cooling. Stirring was continued for 2 h. The ether layer was separated, washed with 5% salt solution, and dried over $CaCl_2$. The ether was removed and the resi-

due was vacuum distilled. Yield, 10 g (44%). Bp 150-151° (3 mm). Found, %: C 57.8, H 5.4, Cl 15.3, S 14.3. $C_{11}H_{13}ClOS$. Calculated, %:C 57.8, H 5.2, Cl 15.6, S 14.0.

2-(p-Tolylmercapto)-5-chloropentanone-4 (IVb). This was synthesized analogously. Yield 45%. Bp 152° (3 mm Hg). Found, %: C 59.2, H 6.0, Cl 14.9, S 13.0. $C_{12}H_{15}ClOS$. Calculated %: C 59.4, H 6.2, Cl 14.6, S 13.2.

2-(p-Chlorophenylmercapto)-5-chloropentanone-4 (IVc). This was synthesized analogously. Yield, 51%. Bp 161-163° (3 mm Hg). Found, %: C 50.6, H 4.3, Cl 27.3, S 12.4. $C_{11}H_{12}Cl_2OS$. Calculated,%:C 50.2, H 4.6, Cl 27.0, S 12.2.

2-Methyl-4-chloromethyl-1-benzothiapyrilum Perchlorate (Va). A mixture of 4.6 g (0.02 mole) of IVa, 6 g (0.022 mole) of triphenylmethyl chloride and 20 ml of 70% perchloric acid in 40 ml of acetic acid was stirred for 3 h at 40°. Then the mixture was poured into 200 ml of ether and thoroughly agitated. The aqueous layer was separated and cooled and the crystalline precipitate was filtered off. Yield, 3.4 g (54.5%). Mp 142-143° (from acetic acid). PMR spectrum (in $CF_3COOH$): 3.50 (3H, s, 2-$CH_3$), 5.50 (2H, s, $CH_2Cl$), 8.33-8.77 ppm (5H, m, $H_{arom}$). Found, %: C 43.3, H 3.2, Cl 22.5, S 10.1. $C_{11}H_{10}Cl_2O_4S$. Calculated, %: C 42.7, H 3.2, Cl 23.0, S 10.0.

2,6-Dimethyl-4-chloromethyl-1-benzothiapyrilium Perchlorate (Vb). This was synthesized analogously. Yield, 60%. Mp 150-151° (from acetic acid). PMR spectrum (in $CF_3COOH$): 2.98 (3H, s, 6-$CH_3$), 3.50 (3H, s, 2-$CH_3$), 5.50 (2H, s, $CH_2Cl$), 8.33-8.70 ppm (4H, m, $H_{arom}$). Found %: C 44.8, H 3.9, Cl 21.5, S 10.2. $C_{12}H_{12}Cl_2O_4S$. Calculated,%:C 44.6, H 3.7, Cl 22.0, S 10.0.

Reaction of Perchlorate Ia with Alkali. To a solution of 12 g (0.032 mole) of Ia in 150 ml of DMFA was added a solution of 3 g of NaOH in 15 ml of water. The resulting solution was held at 90° for 4 h. It was then cooled, poured into 1 liter of cold water and extracted with ether. The extract was dried over $CaCl_2$. The solvent was removed and the residue was extracted with 100 ml of heptane. The solvent was removed and products VIa and VIIa were separated by chromatography on aluminum oxide, with 1:1 benzene–heptane eluent. The course of the chromatography was monitored by GLC. Yield of VIa, 0.67 g (9%). Mp 73-74° (from hexane). IR spectrum: 1690, 1600, 1590, 1460, 1340, 1285, 1230, 1200, 1100, 1000, 955 $cm^{-1}$. PMR spectrum (in $CD_3CN$): 4.3 (2H, s, $CH_2$), 7.1-8.0 ppm (10H, m, $H_{arom}$). Found, %: C 81.0, H 5.4. $C_{16}H_{12}O_2$. Calculated, %: C 81.3, H 5.1.

VIIa was isolated by further elution. Yield, 0.8 g (10%). Mp 81-82° (from hexane). Found, %: C 75.9, H 4.1, Cl 13.7. $C_{16}H_{11}ClO$. Calculated, %: C 75.5, H 4.3, Cl 13.9.

The analogous reaction of perchlorate Ib with aqueous alkali gave: 3-phenacyl-5-methylbenzo[b]furane (VIb); yield, 7%, mp 185-190° (1 mm Hg). IR spectrum: 1690 $cm^{-1}$ (C=O). Found %: C 81.2, H 5.4. $C_{17}H_{14}O_2$. Calculated: C 81.6, H 5.6. 6-Methyl-4-chloromethylflavene (VIIb); yield 12%, mp 93-94°. IR spectrum: 1640, 1600, 1580, 1565, 1325, 1285, 1230, 1135, 1075, 1050, 1030, 910, 870, 820, 795, 765, 700, 685 $cm^{-1}$. Found, %: C 76.5, H 4.3, Cl 13.5. $C_{17}H_{13}ClO$. Calculated, %:C 76.0, H 4.8, Cl 13.2.

## LITERATURE CITED


1. F. Quint, R. Putter, and W. Dilthey, Chem. Ber., 71, 356 (1930).
2. A. T. Balaban and C. D. Nenitzescu, Chem. Ber., 93, 599 (1960).
3. I. Degani and R. Fochi, Ann. Chim., 58, 251 (1968).
4. I. Degani, R. Fochi, and G. Spunta, Bull. Soc. Fac. Chim. Ind. Bologna, 23, 151 (1965).
5. V. I. Dulenko, N. N. Alekseev, V. M. Golyak, and L. V. Dulenko, Khim. Geterotsikl. Soedin., No. 8, 1135 (1977).
6. G. A. Reynolds, J. A. Van Allan, and D. Deniel, J. Heterocycl. Chem., 7, 1395 (1970).
7. B. D. Tilak and G. T. Panse, Indian. J. Chem., 7, 191 (1970).
8. N. S. Zefirov, Mechanisms of Heterocyclic Reactions [in Russian], Nauka, Moscow (1976), p. 113.
9. V. I. Dulenko and V. M. Golyak, Zh. Org. Khim., 16, 1109 (1980).
10. J. A. Van Allan and G. A. Reynolds, Tetrahedron Lett., No. 25, 2047 (1969).
11. J. C. Petropoulos, M. A. McCall, and D. C. Tarbell, J. Am. Chem. Soc., 75, 1130 (1953).