SYNTHESIS OF HETARYL-SUBSTITUTED PYRYLIUM SALTS AND HETARYLPYRIDINES FROM TERTIARY HETEROCYCLIC CARBINOLS

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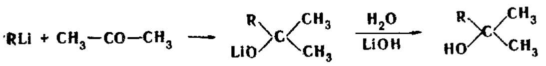
The synthesis of dimethyl benzothiazol-2-yl, 2-thienyl, and 1-methylbenzimidazol-2-yl carbinols and their acylation with acetic anhydride in the presence of perchloric acid have been performed. A method for the synthesis of 4-(benzothiazol-2-yl)-2,6-dimethylpyrylium and 4-(2-thienyl)-2,6-dimethylpyrylium perchlorates has been developed; these substances are converted by treatment with aqueous ammonia into the corresponding 4-(2-hetaryl)-2,6-dimethylpyridines.

Recently, in our laboratory it was discovered that cyclic tertiary alcohols on bisacylation with acid anhydrides in the presence of perchloric acid form pyrylium salts in good yields [1-3]. Heterocyclic tertiary carbinols have not previously been used in this reaction.

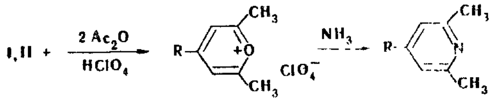
In view of the fact that pyrylium salts with heterocyclic substituents in the γ position are difficult of access, it appeared of interest to synthesize these compounds from tertiary heterocyclic carbinols of the type of $R-C(OH)-(CH_3)_2$, where R is a thiophene, benzothiazole, or 1-methylbenzimidazole residue. The initial heterocyclic tertiary alcohols were obtained by the reaction of the corresponding 2-lithium-substituted heterocycles with acetone.



I-III

I R=benzothiazol-2-yl, II R= 2-thienyl; III R- 1-methylbenzimidazol-2-yl.

To obtain pyrylium salts with heterocyclic substituents in position 4, the 2-hetaryl dimethyl carbinols (I-III) were acylated with acetic anhydride in the presence of perchloric acid. The molar ratio of the reactants carbinol, acetic anhydride, and perchloric acid was 1 : 6 : 1. The dimethyl benzothiazol-2-yl and 2-thienyl carbinols formed 4-(2-hetaryl)-2,6-dimethylpyrylium perchlorates by the usual mechanism of the bisacylation of tertiary carbinols:



IV,V VI,VII

IV, VI R= benzothiazol-2-yl; V, VII R= 2-thienyl.

Compound (IV) proved to be identical with the salt obtained by the reaction of 2,6-dimethyl-γ-pyrone with benzothiazol-2-yllithium followed by treatment with perchloric acid [4].

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Under the action of aqueous ammonia, 4-(benzothiazol-2-yl)-2,6-dimethylpyrylium and 2,6-dimethyl-4-(2-thienyl)pyrylium perchlorates (IV and V) are readily converted into the previously unknown 4-(2-hetaryl)-2,6-dimethylpyridines (VI, VII).

The IR spectra of compounds (IV and V) have characteristic absorption bands of a pyrylium ring and a strong broad band in the 1110-1120-cm^{-1} region (ClO_4 anion) [5, 6].

The reaction of dimethyl 1-methylbenzimidazol-2-yl carbinol with acetic anhydride in the presence of perchloric acid under similar conditions led to the isolation of only traces of 2,6-dimethyl-4-(1-methylbenzimidazol-2-yl)pyrylium perchlorate (VIII), the presence of which was detected spectroscopically.

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument in paraffin oil. The IR spectra of compounds (I-III) each had a broad band in the 3310-3330-cm^{-1} range which is characteristic for the stretching vibrations of an OH group.

Dimethyl 1-Methylbenzimidazol-2-yl Carbinol (III). With vigorous stirring, a solution of 4 g (0.03 mole) of 1-methylbenzimidazole in 10 ml of ether was added to a solution cooled to –75°C of butyllithium obtained from 0.4 g (0.55 g-atom) of lithium and 4 g (0.029 mole) of butyl bromide in 30 ml of dry ether. After 2 h, 2 g (0.034 mole) of acetone was added to the 1-methylbenzimidazol-2-yllithium. The mixture was kept at –75°C for 1 h and then the temperature was brought up to that of the room over an hour. After the end of the reaction, 10-15 ml of water was added. The precipitate of the carbinol (III) that deposited was filtered off. Yield 4.8 g (83.4%). Mp 190-191°C (from a mixture of benzene and petroleum ether). Found, %: C 70.8; H 7.3; N 14.0. $C_{11}H_{14}N_2O$. Calculated, %: C 70.6; H 7.2; N 14.2.

Benzothiazol-2-yl Dimethyl Carbinol (I). As in the preceding case, 0.4 g (0.55 g-atom) of lithium, 4 g (0.029 mole) of butyl bromide, 4.1 g (0.03 mole) of benzothiazole, and 2 g (0.034 mole) of acetone yielded 4.6 g (79.2%) of a carbinol with mp 95-96°C (from benzene–petroleum ether). Found, %: C 61.6; H 5.7; N 7.4. $C_{10}H_{11}NOS$. Calculated, %: C 61.9; H 5.7; N 7.3.

Dimethyl 2-Thienyl Carbinol (II). To the 2-thienyllithium obtained from 0.03 mole of thiophene and butyllithium in a similar manner to the preceding synthesis, metallation being performed for 1 h, was added 2 g (0.034 mole of acetone). The reaction was performed at 20°C for 2 h. The yield of carbinol was 2.7 g (50%). Mp 104-105°C (from benzene–petroleum ether). Found, %: C 58.9; H 7.3; S 22.9. $C_7H_{10}OS$. Calculated, %: C 59.1; H 7.1; S 22.6.

4-(Benzothiazol-2-yl)-2,6-dimethylpyrylium Perchlorate (IV). The acetyl perchlorate from 4.9 g (0.048 mole) of acetic anhydride and 0.8 ml (0.008 mole) of 70% perchloric acid was added to 1.55 g (0.008 mole) of benzothiazol-2-yl dimethyl carbinol. The mixture was boiled for 6 h, the coloration changing from light to dark brown. After the end of the reaction, the excess of ether was poured off. The crystals that had deposited were reprecipitated with ether from acetone. Mp 215-216°C (decomp.). Yield 2 g (74%). A mixture of the substance with a sample synthesized by the method described previously [4] gave no depression of the melting point. Found, %: C 48.86; H 3.7; Cl 10.3; N 4.2; S 10.0. $C_{14}H_{11}NOS \cdot HClO_4$. Calculated, %: C 49.2; H 3.5; Cl 10.3; N 4.0; S 9.4. IR spectrum, cm^{-1}: 1635, 1585, 1505, 1100.

4-(Benzothiazol-2-yl)-2,6-dimethylpyridine (VI). A mixture of 1.6 g (0.03 mole) of (IV) and an excess of 25% ammonia solution was left for 7-8 h. Then the precipitate of (VI) was filtered off and was chromatographed on a column of alumina [benzene–chloroform (3 : 2)]. Yield 0.62 g (85%). Mp 106-107°C. Found, %: C 69.4; H 4.9; N 11.2; S 13.0. $C_{11}H_{12}N_2S$. Calculated, %: C 69.9; H 5.0; N 11.6; S 13.3; picrate, mp 262-263°C (from ethanol). Found, %: N 14.7. $C_{14}H_{12}N_2S \cdot C_6H_3N_3O_7$. Calculated, %: N 14.9.

2,6-Dimethyl-4-(2-thienyl)pyrylium Perchlorate (V). This was obtained in a similar manner to (IV) from 0.71 g (0.005 mole) of (II), 3.06 g (0.03 mole) of acetic anhydride, and 0.5 ml (0.005 mole) of 70% perchloric acid. Yield 0.8 g (55%). Mp 197-198°C (from acetone–ether). Found, %: C 45.0; H 3.6; Cl 11.8; S 10.8. $C_{11}H_{10}OS \cdot HClO_4$. Calculated, %: C 45.4; H 3.8; Cl 12.2; S 11.0. IR spectrum, cm^{-1}: 1610, 1590, 1100.

2,6-Dimethyl-4-(2-thienyl)pyridine (VII) was obtained with a yield of 80%. It was identified in the form of the picrate, with mp 240-241°C (from ethanol). Found, %: C 48.5; H 3.8; N 13.5; S 8.0. $C_{11}H_{11}NS \cdot C_6H_3N_3O_7$. Calculated, %: C 48.8; H 3.4; N 13.4; S 8.0.

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