SYNTHESIS OF 3-ARYL-SUBSTITUTED 2-BENZOPYRYLIUM SALTS WITH A FREE α POSITION

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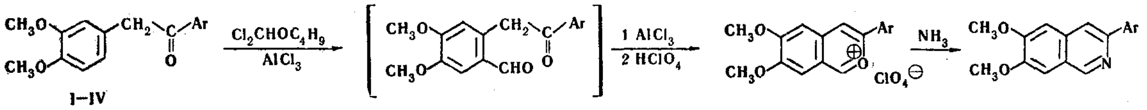
A method for the synthesis of the previously unknown 3-aryl-substituted 6,7-dimethoxy-2-benzopyrylium salts with a free α position by the formylation of 3,4-dimethoxydeoxybenzoins with butyl dichloromethyl ether in the presence of anhydrous $AlCl_3$ has been developed. The pyrylium salts, which were isolated in high yield in the form of stable perchlorates, readily exchange their heteroatom for nitrogen under the action of aqueous ammonia.

In order to synthesize the previously unknown 3-aryl-substituted 2-benzopyrylium salts, we have studied the formylation of alkoxy-substituted deoxybenzoins with butyl dichloromethyl ether in the presence of anhydrous aluminum chloride by Rieche's method [1]. The presence of electron-donating substituents in the meta position of the initial deoxybenzoins substantially facilitates the attack by the formylating agent on the ortho position of the phenol ring, which is isolated from the carbonyl group by a methylene bridge. The 1,5-oxoaldehydes formed cyclize immediately to give 2-benzopyrylium salts containing no substituents in position 1 of the pyrylium ring.



I–IV

I Ar=p-$CH_3OC_6H_4$; II Ar=p-$C_2H_5OC_6H_4$; III Ar=3′,4′-$(CH_3O)_2C_6H_3$; IV Ar=2′,4′-$(CH_3O)_2C_6H_3$

The formylation of the deoxybenzoins (I-IV) with butyl dichloromethyl ether in the presence of $AlCl_3$ takes place under mild conditions (0-20°C) and is carried out by the method that two of us have proposed previously [2]. The 2-benzopyrylium tetrachloroaluminates formed during the reaction are readily converted into crystalline perchlorates by the addition of perchloric acid. The 3-aryl-6,7-dimethoxy-2-benzopyrylium perchlorates obtained by this method were isolated in the pure state with good yields (65-70%).

The compounds synthesized, like other pyrylium salts with a free α or γ position, should possess a high reactivity with respect to nucleophilic addition reactions [3].

In contrast to 1,3-disubstituted 2-benzopyrylium salts unsubstituted in the α position, the isobenzopyrylium salts are converted into the corresponding isoquinolines comparatively readily. Thus, even the action of concentrated aqueous ammonia solution on 3-(4′-ethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium perchlorate gave an 86% yield of 3-(4′-ethoxyphenyl)-6,7-dimethoxy isoquinoline.

The structure of all the salts synthesized was confirmed by IR spectroscopy.

EXPERIMENTAL

4′-Ethoxy-3,4-dimethoxydeoxybenzoin (II). A mixture of 0.98 g (5 mmoles) of homoveratric acid, 0.61 g (5 mmoles) of phenetole and 15 g of polyphosphoric acid was heated at 63-65°C with vigorous stirring for 2 hr. The reaction mixture was poured into 20 ml of cold water and the product was filtered off, washed with water, and dried. Yield 1.2 g (80%), colorless crystals with mp 134°C (ethanol). The other deoxybenzoins were obtained as described previously [4].

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3-(4'-Ethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium Perchlorate. A solution of 1.5 g (5 mmoles) of II in 5-7 ml of methylene chloride was cooled to 0°C and, with stirring, 1.3 g (10 mmoles) of $AlCl_3$ was added, followed, dropwise, by 1.6 g (10 mmoles) of butyl dichloromethyl ether, with continuous stirring. The reaction began immediately with the vigorous evolution of hydrogen chloride, and the reaction mixture became very dark. It was left for 10-15 min until the evolution of HCl had decreased considerably and was poured into a mixture of ice and hydrochloric acid. This led to the formation of the yellow crystalline 2-benzopyrylium tetrachloroaluminate. The subsequent treatment of a suspension of this salt in water with a 70% solution of $HClO_4$ gave a dark yellow crystalline product. Yield 1.4 g (70%), mp 230°C (glacial acetic acid). IR spectrum, cm^{-1}: 1622, 1606, 1244, 1112. Found, %: C 53.2; H 4.7; Cl 8.9. Calculated for $C_{19}H_{19}O_8Cl$, %: C 53.1; H 4.7; Cl 8.6.

3-(4'-Methoxyphenyl)-3-(3',4'-dimethoxyphenyl)-and 3-(2',4'-dimethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium perchlorates were obtained analogously.

3-(4'-Methoxyphenyl)-6,7-dimethoxy-2-benzopyrylium perchlorates, yield 70%, mp 232°C (glacial acetic acid). IR spectrum, cm^{-1}: 1622, 1604, 1240, 1108. Found, %: C 54.2; H 4.4; Cl 8.9. Calculated for $C_{18}H_{17}O_8Cl$, %: C 54.5; H 4.3; Cl 9.0.

3-(3',4'-Dimethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium perchlorates, yield 70%, dark red crystals with mp 240°C (glacial acetic acid). IR spectrum, cm^{-1}: 1646, 1610, 1585, 1230, 1108. Found %: C 53.3; H 4.4; Cl 8.2. Calculated for $C_{19}H_{18}O_9Cl$, %: C 53.6; H 4.2; Cl 8.4%.

3-(2',4'-Dimethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium perchlorate, yield 65%, dark brown crystals with mp 232°C (glacial acetic acid). IR spectrum, cm^{-1}: 1640, 1608, 1582, 1234, 1116. Found, %: C 53.6; H 4.5; Cl 8.4. Calculated for $C_{19}H_{18}O_9Cl$, %: C 53.6; H 4.2; Cl 8.4.

3-(4'-Ethoxyphenyl)-6,7-dimethoxyisoquinoline. An excess of a 22%aqueous solution of ammonia was added to 0.2 g (0.5 mole) of 3-(4'-ethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium perchlorate, and the mixture was left for three days. The light yellow crystals were filtered off, dried, and purified by chromatography on a column of alumina [solvent benzene–chloroform (2:1)]. This gave 0.12 g (86%) of colorless crystals with mp 171°C. Found, %: C 73.9; H 6.2; N 4.5. Calculated for $C_{19}H_{19}NO_3$, %: C 73.8; H 6.2; N 4.5.

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