TETRAPHENYLDIPYRANYL ETHER

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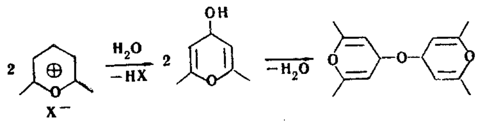
The formation of a dipyranyl ether was observed during a study of the reaction of a γ-unsubstituted pyrylium salt with water in the presence of organic bases. The use, in this reaction, of excess water in conjunction with sodium bicarbonate led to a significant improvement in the synthesis of this ether. The method was extended to the synthesis of dithiapyranyl ether.

Pyrylium salts with free α or γ positions react with nucleophilic reagents at the free position, in contrast to trisubstituted pyrylium salts which react at the α position with nucleophiles. The reaction of α- and γ-unsubstituted pyrylium cations with several aromatic and heterocyclic compounds [1], triphenylphosphine [2, 3], etc., proceeds in this way. The formation of a stable pyranol was expected in the reaction of a γ-unsubstituted pyrylium salt with water. However, the reaction of 2,6-diphenylpyrylium perchlorate with water in the presence of organic bases (pyridine, hexamethylenetetramine) was unexpected and led to the formation of $\alpha,\alpha',\alpha'',\alpha'''$-tetraphenyl-$\gamma,\gamma'$-dipyranyl ether. Thus, a solution of this salt in the presence of pyridine absorbs air moisture, and the dipyranyl ether is formed [4]. The process occurs faster and in higher yields if water is added to the reaction mixture in no more than half of the equimolecular quantity.

At the end of the synthesis (1-2 days) the product is isolated in crystalline form; recrystallization from benzene or toluene, yields red, high-melting crystals that are slightly soluble in alcohol, ether, and soluble in benzene, chloroform, and dimethylformamiede. The structure of the dipyranyl ether was confirmed by the IR spectra and the manner in which the process occurs.

It is most likely that the reaction proceeds through the intermediate formation of 2,6-diphenyl-4-hydroxypyran.



It subsequently was found that replacement of the organic base by aqueous sodium bicarbonate accelerates the process and makes it possible to obtain a final product in higher and more stable yields. This method consists in heating (with vigorous stirring) a suspension of the γ-unsubstituted pyrylium salt in an organic solvent (e.g., benzene) with a slight excess of sodium bicarbonate in the presence of water. Thorough grinding of the solid components accelerates the process. At the end of the reaction (as judged from the disappearance of the pyrylium salt suspension) water is removed from the reaction mixture with a Dean–Stark adapter, the solvent is removed until a small residual volume remains, and the hot benzene solution of the ether is filtered away from the excess sodium bicarbonate and the sodium salt formed, which corresponds to the pyrylium anion. Cooling of the filtrate precipitates the crystalline dipyranyl ether. 2,6-Diphenylthiapyrylium perchlorate is converted to the tetraphenyl dithiapyranyl ether in the same way.

This method of converting pyrylium salts to dipyranyl ethers is similar to the reaction to form ditropyl [5] and dicyclopropenyl [6] ethers from the appropriate salts. However, while ditropyl and dicyclopropenyl ethers are converted to tropylium and cyclopropenylium salts by reaction with mineral acids, this is not characteristic for the dipyranyl ether. The reaction of the compounds under discussion with $HClO_4$ gives an unidentified perchlorate but no 2,6-diphenylpyrylium salt.

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EXPERIMENTAL

$\alpha,\alpha',\alpha'',\alpha'''$-Tetraphenyl-$\gamma,\gamma'$-dipyranyl Ether. A. 2,6-Diphenylpyrylium perchlorate [3.3 g (0.01 mole)] was dissolved in 10 ml of dimethylformamide, and 1 ml of pyridine was added to the solution. One drop of water was added to the mixture with manual stirring, and the resulting mixture was allowed to stand at room temperature for 2 days. The precipitated crystals were filtered, washed with petroleum ether, and dried to give 1.0 g (40%) of a product with mp 216-217° (from toluene). Found %: C 84.6; H 5.2. $C_{34}H_{26}O_3$. Calculated %: C 84.6; H 5.4.

B. Water (1.5 ml) was added to a suspension of 3.3 g (0.01 mole) of pulverized 2,6-diphenylpyrylium perchlorate and 1.5 g of sodium bicarbonate in 70-80 ml of benzene, and the reaction mixture was refluxed with vigorous stirring until the pyrylium salt suspension vanished (~4 h). The condenser was replaced with a Dean–Stark adapter, and water was thoroughly removed from the reaction mixture. Benzene was removed to a final total volume of 15-20 ml and the hot residue was filtered. Cooling of the filtrate gave 1.2 g of a red crystalline precipitate. Another ~0.1 g of product could be isolated by addition of petroleum ether (1:1) to the filtrate. The total yield of product with mp 216-217° (from toluene) was 54%. The analysis of the product was in agreement with the calculated values.

$\alpha,\alpha',\alpha'',\alpha'''$-Tetraphenyl-$\gamma,\gamma'$-dithiapyranyl Ether. This was similarly obtained in 40% yield from 0.01 mole of 2,6-diphenylthiapyrylium perchlorate, 1.5 g of sodium bicarbonate, and 2 ml of water by refluxing the mixture for 12 h. The product had mp 321-322° (from xylene). Found %: C 79.1; H 5.3; S 12.2. $C_{34}H_{26}OS_2$. Calculated %: C 79.5; H 5.1; S 12.4.

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