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Abstract

Full Text

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SYNTHESIS OF PYRYLIUM SALTS BY THE CONDENSATION OF OXYMETHYLENECYCLOHEXANONE WITH KETONES

The method of synthesizing pyrylium salts by the condensation of dicarbonyl compounds with ketones in the presence of acid catalysts is attractive because of its simplicity and accessibility. As has been shown by one of us with co-workers, diketones condense with methyl ketones in the presence of 70% hydrochloric acid to form pyrylium salts in low yields (^1). N. K. Kochetkov and co-workers, in the condensation of acetals of β-ketoaldehydes with phenols, obtained close analogs of natural anthocyanidins in good yields (^2). It has recently been shown that β-chlorovinyl ketones can condense with ketones or enamines to form pyrylium salts (^3,4), while in the condensation of acetophenone with phenylpropionic aldehyde a chalcone is obtained, which in the presence of hydrochloric acid cyclizes to 2,6-diphenylpyrylium perchlorate (^5).

Continuing work on the synthesis of pyrylium salts (^6-8), we have investigated a method for synthesizing the latter on the basis of β-ketoaldehydes. In the condensation of oxymethylenecyclohexanone with various methyl ketones (acetone, acetophenone, p-methoxyacetophenone, α-acetothienone, cyclohexanone, tetralone-1, and others), 5,6,7,8-tetrahydrobenzopyrylium perchlorates substituted in position 2, or octahydroxanthylium salts, are obtained; on treatment with aqueous ammonia these are readily converted into the corresponding sparingly accessible 5,6,7,8-tetrahydroquinolines, or symm. octahydroacridines:

[[chemical scheme: oxymethylenecyclohexanone] + $\frac{H_2C-R_2}{C(=O)-R_1}$ $\xrightarrow{HClO_4}$ [[pyrylium perchlorate intermediate with

The condensation proceeds readily under fairly mild conditions, on brief heating (15–30 min) of oxymethylenecyclohexanone with a 1.5–2-fold excess of ketone and equimolecular amounts of 70% perchloric acid in acetic acid solution. The condensation also proceeds at room temperature, but with lower yields of pyrylium salts. Further increase in the reaction temperature and in the duration of heating does not lead to an increase in the yield of the expected product, but only promotes resinification.

The condensation of ethoxymethylenecyclohexanone (^9) with ketones leads to the formation of pyrylium salts in the same yields as in the case of oxymethylenecyclohexanone. However, in the latter case the reaction proceeds readily already at room temperature. The pyrylium salts obtained are colorless or brightly colored crystalline substances, readily soluble in acetic acid and acetone, but insoluble in low-polarity solvents (benzene, ether). They crystallize well from water; however, prolonged heating in hydroxyl-containing media leads to opening of the pyrylium ring.

The individuality of the synthesized compounds was checked by elemental analysis and by thin-layer chromatography on gypsum (^10) in a toluene : chloroform = 7 : 8 mixture. In the IR spectrum of the synthesized pyrylium salts there are intense absorption bands with a maximum at 1620–

1610 cm^{-1}, which is characteristic of stretching vibrations of C=C bonds of the pyrylium ring ([11]).

Experimental Part

1. Octahydroxanthylium perchlorate. To 2 g (0.016 g-mole) of oxymethylenecyclohexanone in 10 ml of glacial acetic acid are added 1.96 g (0.02 g-mole) of cyclohexanone and 1.6 ml of 70% $HClO_4$. The mixture is heated on a boiling water bath for 30 min; after cooling it is diluted with an equal volume of ether and, after standing for one hour in a refrigerator, 2.5 g (54.4%) of shiny colorless long needles are filtered off. M.p. 155° (from water), R_f 0.18 (toluene : chloroform = 7 : 8). IR spectrum: 1612 cm^{-1}.

Found, %:	C 53.92; H 6.15; Cl 12.51
$C_{13}H_{17}ClO_5$. Calculated, %:	C 54.16; H 5.90; Cl 12.15

On treatment with ammonia, octahydroacridine was obtained in 69.2% yield, m.p. 68°; picrate m.p. 196° (from water). Lit. ([21]): m.p. 69°, picrate 195°.

2. 2-Methyl-5,6,7,8-tetrahydrobenzopyrylium perchlorate. Obtained by the above method from 0.8 g (0.0064 g-mole) of oxymethylenecyclohexanone, 1.5 g of acetone, and 0.7 ml of 70% $HClO_4$. 0.500 g of shiny needles (32.4%) with m.p. 141-143° (from water), R_f 0.95. IR spectrum: 1619 cm^{-1}.

Found, %:	C 48.68; H 5.40; Cl 13.7
$C_{10}H_{13}ClO_5$. Calculated, %:	C 48.38; H 5.24; Cl 14.11

On treatment of the salt with ammonia, 5,6,7,8-tetrahydroquinaldine was obtained in 90% yield, b.p. 225°, picrate m.p. 156°. The constants of the base and picrate agree well with the literature data ([12]).

3. 2-(α-Thienyl)-5,6,7,8-tetrahydrobenzopyrylium perchlorate. From 2 g (0.016 g-mole) of oxymethylenecyclohexanone, 4 g of 2-acetylthiophene, and

1.7 ml of 70% $HClO_4$, 1.2 g (24%) of the salt is obtained in the form of light-green needles with m.p. 188° (from water), R_f 0.22. IR spectrum: 1609 cm^{-1}.

Found, %:	C 49.77; H 4.45; Cl 10.79; S 9.88
$C_{13}H_{13}ClO_5$. Calculated, %:	C 49.40; H 4.11; Cl 11.07; S 10.12

The corresponding 2-(α-thienyl)-5,6,7,8-tetrahydroquinoline was obtained as a colorless oil in 89.4% yield. Picrate m.p. 188°.

4. 2-Phenyl-5,6,7,8-tetrahydrobenzopyrylium perchlorate. From 0.67 g (0.052 g-mole) of oxymethylenecyclohexanone, 1.2 g of acetophenone, and 0.6 ml of 70% $HClO_4$, 0.370 g (23%) of the pyrylium salt is obtained in the form of shiny golden-brown leaflets with m.p. 163–165° (from water), R_f 0.246. IR spectrum: 1617 cm^{-1}.

Found, %:	C 57.72; H 4.85; Cl 10.77
$C_{15}H_{15}ClO_5$. Calculated, %:	C 58.06; H 4.84; Cl 11.29

2-Phenyl-5,6,7,8-tetrahydroquinoline was obtained in 52.4% yield; picrate m.p. 162° (from water).

5. 2-(p-Methoxyphenyl)-5,6,7,8-tetrahydrobenzopyrylium perchlorate. From 2.5 g (0.02 g-mole) of oxymethylenecyclohexanone, 4.5 g of *p*-methoxyacetophenone, and 2 ml of 70% $HClO_4$, 0.9 g (13.2%) of a yellow-green salt is obtained with m.p. 165° (from water), R_f 0.226. IR spectrum: 1618, 1603, 1575, 1563 cm^{-1}.

Found, %:	C 56.37; H 4.92; Cl 10.36
$C_{16}H_{16}ClO_6$. Calculated, %:	C 56.37; H 5.00; Cl 10.29

The picrate of the corresponding 2-(p-methoxyphenyl)-5,6,7,8-tetrahydroquinoline has m.p. 145° (from water).

Found, %:	C 56.95; H 4.36
$C_{22}H_{20}N_4O_8$. Calculated, %:	C 56.41; H 4.27

6. 2-(p-Ethoxyphenyl)-5,6,7,8-tetrahydrobenzopyrylium perchlorate. From 2.5 g (0.02 g-mole) of oxymethylenecyclohexanone,

4.10 g (0.025 g-mole) of *n*-ethoxyacetophenone and 2 ml of 70% $HClO_4$ give 1.8 g (25.4%) of a light-yellow salt with m.p. 185° (from water), R_f 0.258.

Found, %:	C 57.26; H 5.49; Cl 10.06
$C_{17}H_{19}ClO_6$. Calculated, %:	C 57.62; H 5.36; Cl 9.88

structural formula

Figure 1: structural formula

The picrate of 2-(*p*-ethoxyphenyl)-5,6,7,8-tetrahydroquinoline has m.p. 162° (from water).

Found, %:	C 56.73; H 4.61
$C_{23}H_{22}N_4O_8$. Calculated, %:	C 57.26; H 4.57

7. Perchlorate of 2-(3,4-dimethoxyphenyl)-5,6,7,8-tetrahydrobenzopyrylium. From 3.25 g (0.025 g-mole) of oxymethylenecyclohexanone, 5.4 g (0.03 g-mole) of 3,4-dimethoxyacetophenone, and 2.6 ml of 70% $HClO_4$, 1.5 g (15.6%) of a yellow-orange salt with m.p. 177° (from water) is obtained. IR spectrum: 1619, 1598, 1548 cm^{-1}.

Found, %:	C 54.12; H 5.08; Cl 9.10
$C_{17}H_{19}ClO_7$. Calculated, %:	C 55.13; H 5.13; Cl 9.58

The picrate of 2-(3,4-dimethoxyphenyl)-5,6,7,8-tetrahydroquinoline has m.p. 175° (from water).

8. Perchlorate of 7,8-benzoctahydroxanthylium. From 1.5 g (0.012 g-mole) of oxymethylenecyclohexanone, 2.96 g (0.02 g-mole) of tetralone-1, and 1.3 ml of 70% $HClO_4$, 0.400 g (10.2%) of a light-brown salt with m.p. 153° (from acetic acid), R_f 0.387, is obtained.

Found, %:	C 60.10; H 5.13; Cl 10.45
$C_{17}H_{17}ClO_5$. Calculated, %:	C 60.71; H 5.05; Cl 10.41

The pyrylium salt has the structure:

9. Perchlorate of 2,3-cyclopentano-5,6,7,8-tetrahydrobenzopyrylium. From 0.6 g (0.0048 g-mole) of oxymethylenecyclohexanone, 1.26 g of cyclopentanone (0.015 g-mole), and 0.5 ml of 70% $HClO_4$, 0.300 g (23%) of a colorless crystalline salt with m.p. 127–128° (from water), R_f 0.77, is obtained. IR spectrum: 1617, 1584 cm^{-1}.

Found, %:	C 52.93; H 5.65; Cl 13.07
$C_{12}H_{15}ClO_5$. Calculated, %:	C 52.55; H 5.47; Cl 12.92

The product has the structure:

structural formula

Figure 2: structural formula

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Note: Figure translations are in progress. See original paper for figures.