Cycloaddition reaction of 3,4-dihydro-6,7-dimethoxyisoquinoline to pyrylium salts

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The first example of cycloaddition to the 2 and 5 positions of 2,4,6-triphenylpyrylium has been observed.

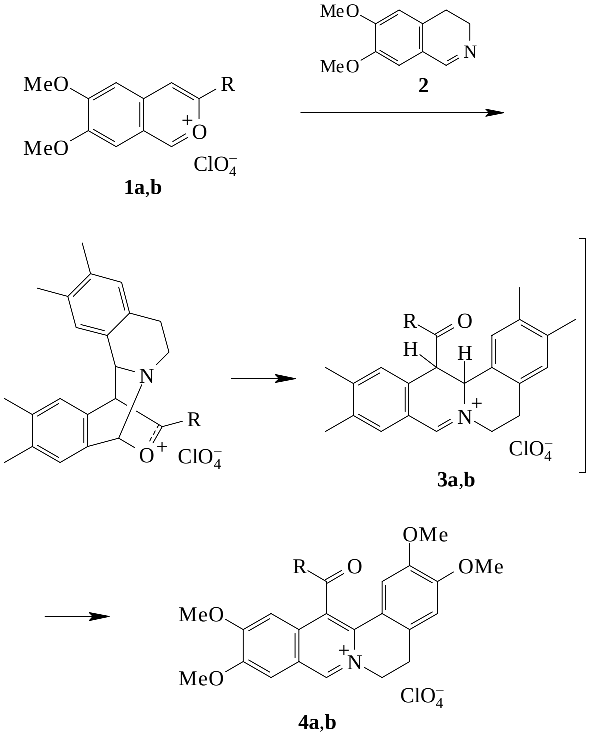
It is known that azomethines undergo cycloaddition reactions with benzo[*c*]pyrylium salts with the formation of dihydroisoquinolinium salts, whose ring includes a C–N fragment from azomethine.[1,2] In contrast, interaction of monocyclic pyrylium salts with azomethines produce pyridinium salts, the same as those obtained from treatment of pyrylium salts with amines from azomethines.[3,4]

Unexpectedly we found that cyclic azomethine (3,4-dihydro-6,7-dimethoxyisoquinoline **2**) interacts by the cycloaddition not only with benzo[*c*]pyrylium salts **1a**,**b** but also with triphenylpyrylium perchlorate **5**.

Treatment of the salt **1a** with **2** in boiling DMF results in the formation of 55% of perchlorate **4a**, separated from the reaction mixture by the addition of diethyl ether and crystallisation of the residue from ethanol. In the same way quinolizinium salt **4b** was obtained in 45% yield.

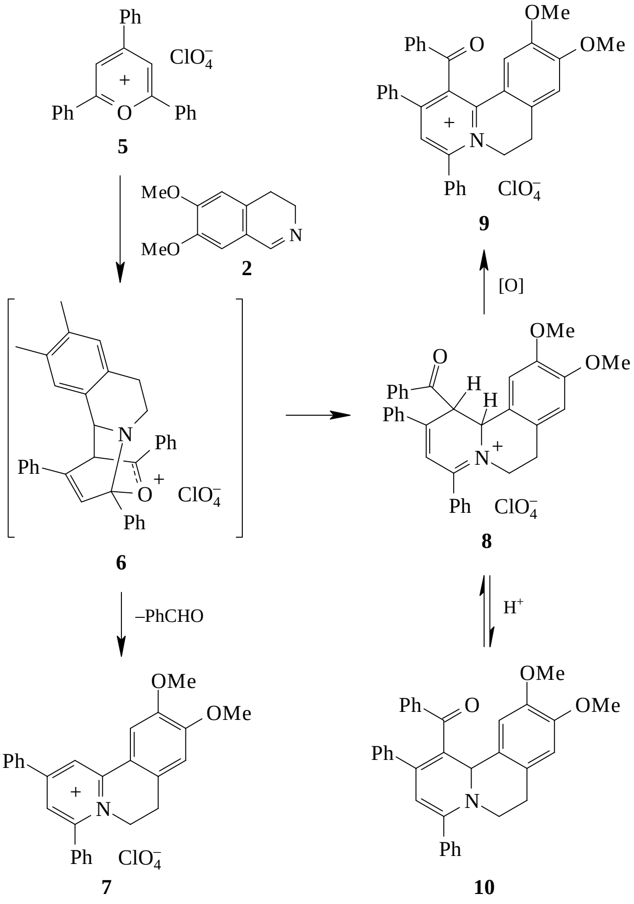
From our point of view, the mechanism of the formation of the salts **4a**,**b** is the same as that for the reaction of benzo[*c*]pyrylium salts with azomethines of aromatic aldehydes.[1] It includes cycloaddition of the C=N double bond to the 1 and 4 positions of the pyrylium ring, followed by cleavage of the ring with oxonium atom. Dihydroquinolizinium salts **3a**,**b**, which have to be the products of this reaction, undergo oxidation under these reaction conditions, Scheme 1.

At the same time, heating of **5** with **2** in DMF for 5 min produce 15% of the salt **7** and 45% of the salt **9**, which were separated by means of column chromatography ($Al_2O_3/CHCl_3$). The same reaction in ethanol yields, in addition to 15% of the salt **7** and 30% of **9**, 20% of a deep-red coloured compound **10** which on treatment with perchloric acid undergoes reverse protonation into the dihydro salt **8**.



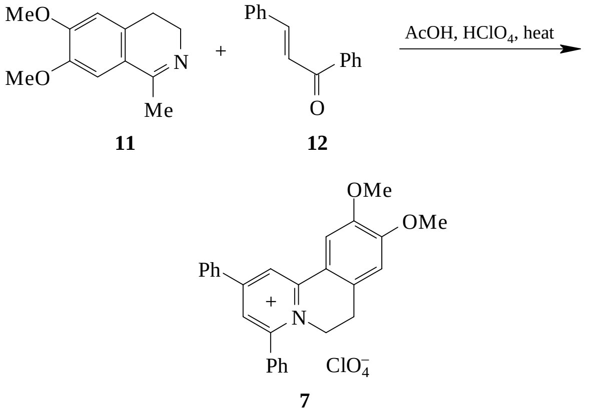
1–4 **a** R = 3,4-$(MeO)_2C_6H_3$
b R = OMe

Scheme 1



Scheme 2

The most reasonable mechanism for this interaction involves cycloaddition of 3,4-dihydro-6,7-dimethoxyisoquinoline **2** to the pyrylium ring, as shown in Scheme 2, with the formation of



Scheme 3

key intermediate **6**. Further elimination of benzaldehyde leads to the aromatic salt **7**, while cleavage of the ring with oxonium atom results in the formation of dihydro salt **8**, which then undergoes oxidation into the salt **9**.

The structures of the salts **4a**,**b** and **7**–**9** were confirmed by means of elemental analysis, IR, ^{1}H NMR spectroscopy and of compound **10** by mass spectroscopy.[†] In addition, the structure of **7** was confirmed by an alternative preparation. Heating of 1-methyl-3,4-dihydro-6,7-dimethoxyisoquinoline **11** with 1,3-diphenylprop-2-enone **12** in acetic acid for 12 h followed by 20 min heating in the presence of a double excess of perchloric acid gave 17% of dihydroquinolizinium salt **7**.

In conclusion, we have found the first example of a recyclisation reaction of monocyclic pyrylium salts *via* cycloaddition of the reagent to the 2 and 5 positions of the pyrylium ring. All well-known recyclisation reactions of monocyclic pyrylium salts[5] are of the so-called ANRORC-type,[6] *e.g.* the main steps in their mechanism involve the nucleophilic addition, ring opening and ring closure.

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[†] *Spectral data*. **4a**: ^{1}H NMR (CDCl$_3$) δ: 3.08 (1H, t, J = 7.5 Hz, CH$_2$), 3.20 (1H, t, J = 7.5 Hz, CH$_2$), 3.37 (3H, s, OCH$_3$), 3.82 (3H, s, OCH$_3$), 3.86 (3H, s, OCH$_3$), 3.90 (3H, s, OCH$_3$), 4.03 (3H, s, OCH$_3$), 4.10 (3H, s, OCH$_3$), 4.68 (1H, t, J = 7.5 Hz, CH$_2$), 5.63 (1H, t, J = 7.5 Hz, CH$_2$), 6.71–7.68 (7H, m, CH$_{ar}$), 9.23 (1H, s, H-1). IR (ν/cm^{-1}): 1660, 1606, 1115; mp 268 °C.

4b: ^{1}H NMR (CF$_3$COOD) δ: 3.18–3.43 (2H, m, CH$_2$), 3.05 (3H, s, OCH$_3$), 3.75 (3H, s, OCH$_3$), 3.80 (3H, s, OCH$_3$), 3.90 (3H, s, OCH$_3$), 4.05 (3H, s, OCH$_3$), 4.65–4.87 (2H, m, CH$_2$), 7.15 (1H, s, CH$_{ar}$), 7.40 (1H, s, CH$_{ar}$), 7.52 (1H, s, CH$_{ar}$), 7.70 (1H, s, CH$_{ar}$), 9.35 (1H, s, H-1). IR (ν/cm^{-1}): 1713, 1606, 1126; mp 245 °C.

7: ^{1}H NMR (CDCl$_3$) δ: 3.06 (2H, t, J = 6.0 Hz, CH$_2$), 3.92 (3H, s, OCH$_3$), 3.96 (3H, s, OCH$_3$), 4.42 (2H, t, J = 6.0 Hz, CH$_2$), 6.86–7.85 (14H, m, CH$_{ar}$). IR (ν/cm^{-1}): 1620, 1220, 1100; mp 251 °C.

8: ^{1}H NMR (CDCl$_3$) δ: 2.45–2.70 (2H, m, CH$_2$), 3.55 (3H, s, OCH$_3$), 3.87 (3H, s, OCH$_3$), 4.20–4.47 (2H, m, CH$_2$), 5.72 (1H, d, J = 6.5 Hz), 6.05 (1H, d, J = 6.5 Hz), 7.07–7.67 (18H, m, CH$_{ar}$). IR (ν/cm^{-1}): 1687, 1663, 1100; mp 141 °C.

9: ^{1}H NMR (CDCl$_3$) δ: 2.65–3.30 (2H, m, CH$_2$), 3.26 (3H, s, OCH$_3$), 3.81 (3H, s, OCH$_3$), 4.30–4.65 (2H, m, CH$_2$), 6.76–7.95 (18H, m, CH$_{ar}$). IR (ν/cm^{-1}): 1673, 1595, 1100; mp 192 °C.

10: Ms: 77 (70) Ph, 105 (100) PhCO, 394 (77) [M – PhCO], 496 (41) [M – 3H], 399 (19) M$^+$.