

Studies of Flavylium Compounds

6. On the Condensation of *o*-Hydroxybenzaldehydes with 2-Acethiothienone and 3-Acethionaphthenone

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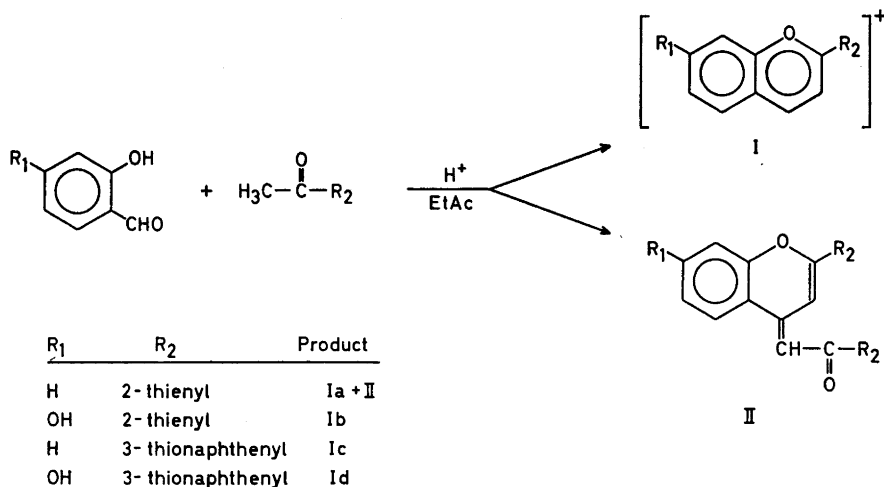
As earlier reported 4-phenacylidene-flavene and not the expected flavylium compound is mainly formed when salicylaldehyde is condensed with some acetophenones with hydrogen chloride as condensing agent.¹ In order to investigate if this side reaction also occurs when heterocyclic ketones are used we have investigated the products formed with some sulphur containing ketones.

Analogously to acetophenone, 2-acethiothienone was found to react with β -resoreylaldehyde forming 7-hydroxy-2-(2'-thienyl)-benzopyrylium chloride (I b), whereas with salicylaldehyde a tarry mixture was obtained. Since it was rather difficult to isolate pure products from this mixture, it was analysed by mass spectrometry. The mass spectrum showed peaks at m/e 336 (28%), and 213 (100%). The

peak at m/e 336 corresponds to the parent ion of the thienacylidenebenzopyrene (II).

The base peak m/e 213 corresponds to the 2-(2'-thienyl)-benzopyrylium ion (I a). It is probably not formed from II since at least two similar compounds, 4'-nitro-4-(*p*-nitrophenacylidene)-flavene and 4'-chloro-4-(*p*-chlorophenacylidene)-flavene do not give any peaks indicating the presence of the corresponding flavylium ions. The molecular ion at m/e 213 was also the base peak in the mass spectrum of the 2-thienyl-benzopyrylium chloride, prepared from the corresponding chalcone. Evidently the condensation of salicylaldehyde and 2-acethiothienone gives both compounds, indicating that in this case the reaction leading to the benzopyrylium chloride is more favoured than when acetophenone is used. The 3-acethiothienone showed behaviour similar to that of the 2-analogue, giving mainly tarry products. However, the presence of the two condensation products was shown by mass spectrometry.

3-Acethionaphthenone gave on condensation with β -resoreylaldehyde, as well as with salicylaldehyde, the corresponding benzopyrylium compounds (I c and I d) and no trace of the side reaction product could be detected in the mass spectra of the condensation products. One possible explanation of the absence of a compound of type II when salicylaldehyde is used might be that the steric requirements of the thionaphthenyl part to some extent prevent the planarity of the molecule. The 3-



acetothionaphthenone is also more stable under the condensation conditions than the acetothienones and pure products are easily formed therefrom.

Experimental. The UV spectra were measured in methanol containing 0.01 % conc. HCl with a Bausch and Lomb Spectronic 505 spectrophotometer and the infrared spectra in the KBr phase with a Perkin-Elmer spectrophotometer. The mass spectra were measured with an LKB 9000 instrument.

The condensations were performed by saturating a solution of equimolecular amounts of the aldehyde and the ketone in dry ethyl acetate at 0° with dry hydrogen chloride.

2-(2'-Thienyl)-benzopyrylium chloride (I a) (perchlorate³) was prepared in two ways.

(1) from *o*-hydroxybenzylidene-2-acetothienone³ by ring closure in dry ethyl acetate with hydrogen chloride. The benzopyrylium chloride was precipitated with ether and washed with ether. UV: λ_{\max} 436 nm. IR: ν_{\max} 1618 cm^{-1} . MS: *m/e* 213 (100 %), 184 (9 %), 152 (7 %), 111 (18 %), 36 (33 %).

(2) from salicylaldehyde and 2-acetothienone. After precipitation with ether the reaction product was purified by repeated precipitation from methanolic HCl with ether. UV: λ_{\max} 263, 282, 434 nm. IR: ν_{\max} 1618, 1650 cm^{-1} .

PC on Whatman No. 1 in butanol-2 N HCl (1:1 v/v, upper phase) gave two spots, one reddish and one orange-yellow (R_F 0.52 and 0.75). The first spot was identical with the compound obtained according to the first method.

7-Hydroxy-2-(2'-thienyl)-benzopyrylium chloride (I b) obtained from β -resorecylaldehyde and 2-acetothienone was purified by solution in formic acid, saturated with HCl and precipitation with ether. UV: λ_{\max} 467 nm. IR: ν_{\max} 1630 cm^{-1} . MS: *m/e* 229 (21 %), 228 (36 %), 200 (42 %), 171 (36 %), 111 (14 %), 36 (100 %). (Found: C 58.82; H 3.54; Cl 12.70; S 11.03. Calc. for $\text{C}_{13}\text{H}_9\text{ClO}_2\text{S}$ (264.7): C 58.98; H 3.43; Cl 13.40; S 12.11).

2-(3'-Thionaphthenyl)-benzopyrylium chloride (I c) was prepared in two ways.

(1) from *o*-hydroxybenzylidene-3-acetothionaphthenone. This compound was prepared by condensation of 3-acetothionaphthenone with salicylaldehyde in ethanol by means of KOH. After recrystallisation from ethanol the chalcone melted at 152–153°C. IR: ν_{\max} 1640 cm^{-1} . MS: *m/e* 280 (66 %), 263 (55 %), 161 (100 %), 134 (56 %), 89 (68 %). (Found: C 72.72; H 4.26; S 11.49. Calc. for $\text{C}_{17}\text{H}_{12}\text{O}_2\text{S}$ (280.3): C 72.83; H 4.32; S 11.44).

Ring closure to the benzopyrylium chloride was performed in dry dioxane with hydrogen chloride. Purification was performed by repeated washing with ether. UV: λ_{\max} 259, 291, 299, 459 nm. IR: ν_{\max} 1622 cm^{-1} . MS: *m/e* 263 (39 %), 262 (38 %), 36 (100 %). (Found: C 60.00; H 3.59; Cl 20.54; S 9.52. Calc. for $\text{C}_{17}\text{H}_{11}\text{ClOS}$ (298.8) + 1 mole HCl: C 60.20; H 3.61; Cl 21.14; S 9.57).

(2) from salicylaldehyde and 3-acetothionaphthenone. The purified reaction product proved to be I c and gave the same spectral data as above.

7-Hydroxy-2-(3'-thionaphthenyl)-benzopyrylium chloride (I d) from β -resorecylaldehyde and 3-acetothionaphthenone was purified by washing with ether. UV: λ_{\max} 250, 265, 335, 478 nm. IR: ν_{\max} 1630 cm^{-1} . (Found: 64.39; H 3.55; S 9.78; Cl 11.34. Calc. for $\text{C}_{17}\text{H}_{11}\text{ClO}_3\text{S}$ (314.8): C 64.87; H 3.52; S 10.19; Cl 11.26).

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