

Synthesis of Boron-containing Complexes of 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one

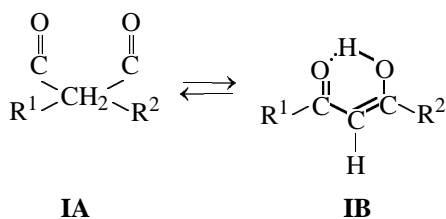
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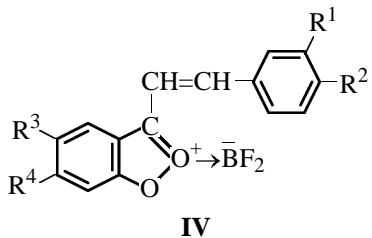
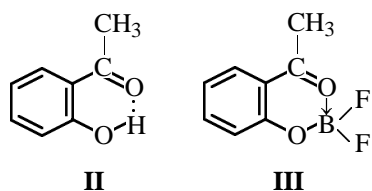
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Abstract—Condensation of *o*-hydroxyacetophenone with benzaldehyde in alcohol in the presence of a triple excess of a sodium hydroxide solution leads to 2'-hydroxychalcone sodium salt. The latter was heated with boron trifluoride etherate in toluene to a 2'-hydroxychalcone boron fluoride complex in which the boron atom is coordinated to the carbonyl oxygen atom. The same complex was obtained by boiling of the *o*-hydroxyacetophenone boron fluoride complex with benzaldehyde in acetic anhydride.

Complex formation of β -diketones with transition metal salts and boron compounds have previously been widely studied [1–3]. The complex-forming ability of β -diketones is primarily associated with their tendency for tautomerization into the keto-enol form containing an intramolecular hydrogen bond (IA \rightleftharpoons IB).



2-Hydroxyacetophenone (II) can be considered as a β -diketone in a fixed keto-enol form. It was earlier shown [4] that 2-hydroxyphenone reacts with boron trifluoride to give complex III.

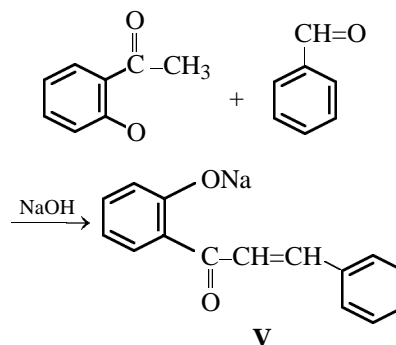


However, recently Panasenko and Starkov [5] reported the synthesis of boron trifluoride complexes

of chalcones derived from substituted 2-hydroxyacetophenones, which were assigned structure IV.

This assignment casts some doubt, since it is well known that β -diketonate ligands tend to form a six-membered chelate ring [1]. In this connection and proceeding with our works in the field of boron-containing complexes with bidentate ligands, we turned to complex formation of 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one with boron trifluoride etherate.

2'-Hydroxychalcone was prepared as sodium salt V by condensation of 2-hydroxyacetophenone with benzaldehyde in ethanol in the presence of a triple excess of a sodium hydroxide solution [6].

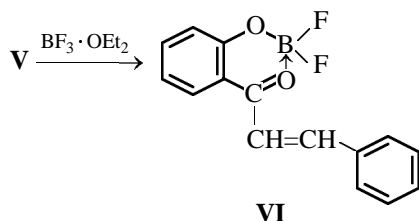


We did not try to isolate chalcones in the free state, knowing [7] that on acidification of their alkaline solutions these compounds may cyclize into the corresponding flavones.

The presence of sodium in the product was proved a flame reaction. Compound V is readily soluble in water and almost insoluble in organic solvents. Its structure was confirmed by spectral methods.

Thus, the IR spectrum contains a band at 1655 cm^{-1} , characteristic of chalcone $\nu(\text{C}=\text{O})$ and $\nu(\text{CH}=\text{CH})$ stretching vibrations [8]. The ^1H NMR spectrum of compound **V** displays at 6.40 and 6.88 ppm doublets of olefin protons with a coupling constant of 18.2 Hz, which implies an *E* configuration of this compound [9].

Compound **V** was brought into condensation with boron trifluoride etherate without additional purification. The complex formation was effected by boiling equimolar amounts of **V** and boron trifluoride etherate in toluene for 4–5 h. The reaction mixture was filtered while hot, after which the solvent was removed in a vacuum, and the product was recrystallized from benzene.

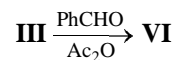


We assigned structure **VI** to the resulting complex, relying on the following evidence. The complex turns the flame to an intense green color, which is characteristic of boron-containing compounds. The chalcone $\nu(\text{C}=\text{O})$ band is shifted red by 15 cm^{-1} , suggesting involvement of the oxygen atom in complex formation. Similar shift is observed in going from 2-hydroxyacetophenone to its boron fluoride complex **III**. Moreover, the IR spectrum of complex **VI** shows new, compared with ligand **V**, bands at 1150–1200 and 1050–1100 cm^{-1} , characteristic of stretching vibrations of B–O and B–F bonds in the chelate entity. Similar bands are observed in the IR spectra of boron fluoride β -diketone complexes [10]. All signals in the ^1H NMR spectrum of complex **VI** are shifted downfield compared with ligand **V**, which is associated with the electron-acceptor nature of the chelate entity. Therewith, the olefin proton signals get closer together but preserve their pattern (doublets at δ 7.07 and 7.10 ppm, *J* 18.0 Hz), implying that the olefin moiety has preserved its *E* configuration.

The electronic absorption spectrum of complex **VI** differs from the spectrum of ligand **V** in that it contains a new band as an inflection at 360–390 nm. Graphical resolution of the experimental absorption curve shows that this band has its maximum at 376 nm with an intensity of $\sim 4000\text{ mol l cm}^{-1}$.

Further evidence for the structure of complex **VI** was obtained by the independent synthesis of this compound by the condensation of the boron fluoride

o-hydroxyacetophenone complex (**III**) with benzaldehyde under reflux in acetic anhydride. Both products had the same physicochemical characteristics.



EXPERIMENTAL

The IR spectra were obtained on a Specord IR spectrophotometer for suspensions in Vaseline oil. The electronic absorption spectra were measured on an M-80 spectrophotometer in ethanol for 10^{-4} solutions. The ^1H NMR spectra were taken on a Bruker spectrometer (200 MHz) in deuteriochloroform; internal reference TMS. Thin-layer chromatography was performed on Silufol plates.

Boron fluoride *o*-hydroxyacetophenone complex (III). Boron trifluoride etherate, 4.40 g, was added to a solution of 3.20 g of *o*-hydroxyacetophenone in 25 ml of dry benzene, and the mixture was heated for 60 min at 40–50°C. After cooling, the precipitate was filtered off and washed with benzene to obtain 3.13 g (71%) of complex **III**, mp 141–143°C {published data [4]: mp 142.5–145.0°C}.

(2-Hydroxyphenyl)-3-phenyl-2-propen-1-one sodium salt (V). Sodium hydroxide, 3.85 g (30% solution, 9 ml), was added to 3.20 g of 2-hydroxyacetophenone and 2.50 g of benzaldehyde in 30 ml of ethanol at 40–50°C. The mixture was stirred for 20 min and cooled to room temperature. The precipitate that formed was filtered off, washed with benzene, and dried over calcium chloride to obtain 5.20 g (97%) of compound **V** that was used in subsequent reactions without additional purification. IR spectrum, ν , cm^{-1} : 1655 (C=O + CH=CH), 1595, 1538, 1320, 1187, 987, 880. Electronic absorption spectrum, λ_{max} , nm (ϵ): 319 (7200), 251 (9300). ^1H NMR spectrum, δ , ppm: 6.02 d (1H), 6.40 d (1H), 6.88 d (1H), 6.91 t (1H), 7.00–7.20 m (5H), 7.48 t (1H), 7.87 d (1H).

Complex formation of chalcone V with boron trifluoride etherate. Boron trifluoride etherate, 9.50 g, was added with vigorous stirring to 30 ml of toluene in 5.20 g of compound **V**. The mixture was heated at 75–80°C for 4 h, after which it was filtered while hot, cooled, filtered once more, the solvent was removed in a vacuum, and the residue was recrystallized from benzene to obtain 1.28 g (81%) of compound **VI**, mp 242–243°C {published data [5]: mp 242–244°C}. IR spectrum, ν , cm^{-1} : 1630 (C=O + CH=CH), 1575, 1520, 1250, 1180 (BF₂), 1130 (BF₂), 1080 (BF₂), 1050 (BF₂). Electronic absorption spectrum, λ_{max} , nm (ϵ): 360–390 (4200), 318 (11300). ^1H NMR spectrum

(acetone- d_6), δ , ppm: 7.02 d (1H), 7.07 d (1H), 7.10 d (1H), 7.13 t (1H), 7.40–7.60 m (5H), 7.91 t (1H), 8.15 d (1H).

Condensation of complex III with benzaldehyde.

Benzaldehyde, 1.06 g, was added to a solution of 1.54 g of complex III in 20 ml of acetic anhydride. The mixture was heated at 75–80°C for 2 h, cooled, and left to stand for 1 day. The precipitate that formed was filtered off, the filtrate was vacuum-evaporated, and the solid residue was combined with the precipitate to obtain 1.60 g (59%) of the reaction product, mp 241–243°C (from benzene). The physicochemical constants of this compound were coincident with those of the condensation product of chalcone V with boron trifluoride etherate.

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