

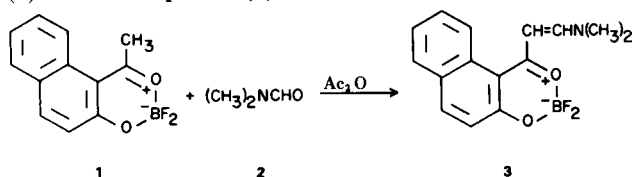
The Reactions of 2,2-Difluoro-4-methylnaphtho[1,2-*e*]-1,3,2-dioxaborin
and Its [2,1-*e*] Isomer with *N,N*-Dimethylformamide

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The title compounds react with dimethylformamide in acetic anhydride to give dimethylamino-vinyl derivatives which, on treatment with base, yield benzochroman-4-ones. The [1,2-*e*] isomer reacts with the Vilsmeier complex to give 3-formylbenzo[*f*]chrom-4-one and 9-hydroxy-1-phenalenone, and the [2,1-*e*] isomer gives 3-formylbenzo[*h*]chrom-4-one.

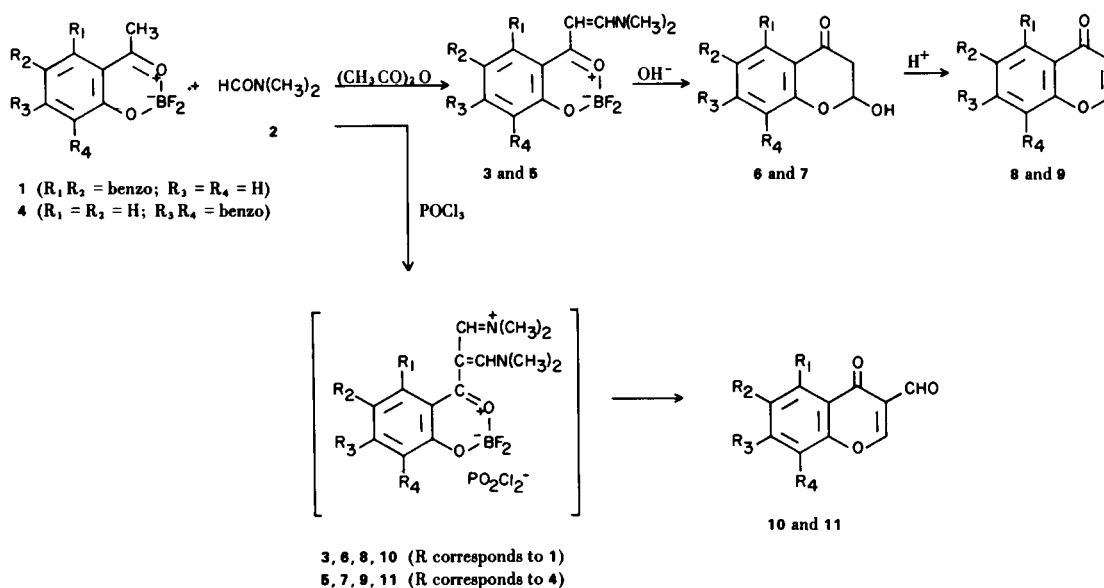
The reaction of 2,2-difluoro-4-methylnaphtho[1,2-*e*]-1,3,2-dioxaborin (**1**) with *N,N*-dimethylformamide (**2**) in acetic anhydride to give the dimethylaminovinyl derivative (**3**) has been reported (1).



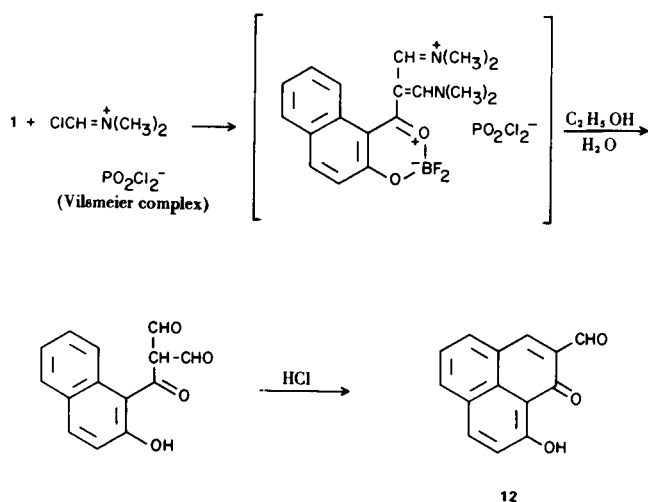
The present paper describes the extension of this reaction to the 2,1-*e* isomer (**4**), the reactions of **1** and **4** with **2** and phosphorous oxychloride (Vilsmeier complex), and the hydrolysis of the products obtained by these reactions.

The reactions of **1** and **4** with **2** are similar to those of methylpyrylium salts (**2**) in that the products obtained in acetic anhydride (**3** and **5**) are derived from equivalent amounts of the starting materials (mono-adducts), and those obtained from the Vilsmeier complex (**10**, **11** and **12**) are formed from one equivalent of the active methyl compound and two equivalents of the complex (bis-adducts). In contrast to the pyrylium bis-adducts, the dioxaborin bis-adducts are unstable and their hydrolysis products are isolated from the reaction mixture. The mono-adducts (**3** and **5**) are hydrolyzed by base to the 2-hydroxy-4-chromanone derivatives (**6** and **7**) which, in turn, are dehydrated with acid to the 4-chromones (**8** and **9**). These reactions are shown in Scheme I.

SCHEME I



The product obtained by the reaction of **4** with the Vilsmeier complex was **11**. However, **10** was a minor product from **1**. The major product was the phenalenone derivative (**12**), which was formed by ring closure of an aldehyde group at a carbon atom. The cyclization is presumably catalyzed by the hydrogen chloride which is liberated from the hydrolysis of the excess Vilsmeier complex. The structure of **12** was proved by decarbonylation to the known 9-hydroxy-1-phenalenone (**3**).



EXPERIMENTAL

Compounds **1**, **3** and **4** were prepared as previously described (1).

2,2-Difluoro-4-(2-dimethylaminovinyl)naphtho[2,1-e]-1,3,2-dioxaborin (**5**).

A mixture of 5 g. of **4**, 3 ml. of *N,N*-dimethylformamide, and 25 ml. of acetic anhydride was refluxed for 10 minutes and cooled. Recrystallization of the resulting solid from acetic anhydride gave 3.3 g. of **5**, m.p. 300-301°; λ_{max} ($\epsilon \times 10^{-3}$) in acetonitrile, ~245 (3.4), 272 (70.8), 338 (18.0), 355 (22.4), 398 (35.6), 416 μ (37.3).

Anal. Calcd. for $C_{15}H_{14}BF_2NO_2$: C, 62.3; H, 4.9; N, 4.8. Found: C, 61.9; H, 4.8; N, 4.6.

2-Hydroxybenzo[*f*]chroman-4-one (**6**).

A mixture of 2 g. of **3** and 25 ml. of 5% methanolic potassium hydroxide was heated on a steam bath for 15 minutes, chilled, and the solid was collected and dissolved in 10 ml. of water. The solution was acidified with acetic acid, and the solid which separated was collected and recrystallized from toluene to give 0.9 g. of product, m.p. 153-154°. The nmr absorption at 60 mHz (dimethylsulfoxide- d_6) showed an ABX pattern with the AB centered at δ 3 (J_{AB} = 21 Hz) (2H) and the X centered at δ 5.92 (1H); a multiplet for the aromatic protons δ 7.1-8.2 (5H) and a doublet centered at δ 9.3 ppm. for the aromatic proton in the 5-position.

Anal. Calcd. for $C_{13}H_{10}O_3$: C, 72.9; H, 4.7. Found: C, 73.2; H, 4.6.

2-Hydroxybenzo[*h*]chroman-4-one (**7**).

Compound **5** was hydrolyzed by the procedure described for

the preparation of **4** to give 1.1 g. of **7**, m.p. 159-160° (from a mixture of petroleum ether and ethanol). The nmr absorption at 60 mHz (dimethylsulfoxide- d_6) showed an ABX pattern with the AB centered at δ 3.03 (J_{AB} = 17 Hz) (2H) and the X centered at δ 6.01 (1H), and a multiplet for the aromatic protons δ 7.4-8.5 ppm. (6H).

Anal. Calcd. for $C_{13}H_{10}O_3$: C, 72.9; H, 4.7. Found: C, 73.1; H, 5.0.

Benzo[*f*]chrom-4-one (**8**).

A mixture of 1.3 g. of **6**, 35 ml. of benzene, and 0.2 g. of *p*-toluenesulfonic acid was refluxed for 0.5 hour, cooled, washed with dilute sodium bicarbonate solution, dried, and the solvent was removed. The residue was recrystallized from petroleum ether to give 0.9 g. of **8**, m.p. 100-101°. The ir absorption was identical to that of a sample prepared by a published procedure (4). The nmr absorption at 60 mHz (deuteriochloroform) showed a doublet at δ 6.04 for the proton at the 3-position (1H), a doublet at 7.8 for the proton at the 2-position (1H), a multiplet δ 7.36-8.01 for 6 of the aromatic protons, and a doublet at δ 10.83 ppm for the aromatic proton at the 5-position.

Anal. Calcd. for $C_{13}H_8O_2$: C, 79.6; H, 4.1. Found: C, 79.5; H, 4.0.

Benzo[*h*]chrom-4-one (**9**).

Compound **7** was dehydrated by the procedure used for the preparation of **8** to give 1 g. of **9**, m.p. 120-121° (from ligroin, b.p. 100-115°). The nmr (deuteriochloroform) showed a doublet at δ 6.4 (1H) for the proton at the 3-position and a multiplet δ 7.5-8.45 ppm (7H) for the aromatic protons including the proton at the 2-position.

Anal. Calcd. for $C_{13}H_8O_2$: C, 79.6; H, 4.1. Found: C, 79.3; H, 4.3.

3-Formylbenzo[*h*]chrom-4-one (**11**).

To 25 ml. of cold *N,N*-dimethylformamide was slowly added 5 ml. of phosphorous oxychloride with swirling, followed by 3 g. of **4**. The mixture was heated on the steam bath for 0.5 hour and poured into 100 ml. of water. The solid was collected and recrystallized from alcohol to give 2.5 g. of **11**, m.p. 160-161°. The nmr (deuteriochloroform) showed a singlet at δ 8.57 (1H) for the proton at the 2-position, a multiplet δ 7.57-8.42 (6H) for the aromatic protons, and a singlet at δ 10.5 ppm for the aldehyde proton.

Anal. Calcd. for $C_{14}H_8O_3$: C, 75.0; H, 3.6. Found: C, 74.7; H, 3.6.

3-Formylbenzo[*f*]chrom-4-one (**10**) and 2-formyl-9-hydroxyphenalenone (**12**).

The Vilsmeier complex was prepared from 30 ml. of *N,N*-dimethylformamide and 15 ml. of phosphorous oxychloride; 10 g. of **1** was added to the complex. After the mixture had been stirred for 10 minutes, a solid separated. The mixture was heated on a steam bath until the solid dissolved; the solution was stirred without heating for 0.5 hour, and diluted with 50 ml. of alcohol followed by 100 ml. of water. The solid was removed by filtration, washed with water, and suspended in 100 ml. of chloroform. The suspension was stirred and a solution of 15 g. of sodium hydroxide in 200 ml. of water was added. The mixture was stirred for 15 minutes and the red, insoluble sodium salt of **12** was collected, dissolved in 100 ml. of boiling acetic acid, and the solution was diluted with a little water and cooled to give 6.2 g. of **12**, m.p. 205-206°.

The aqueous phase from the filtrate of the reaction mixture was acidified with acetic acid, and the resulting solid recrystallized

from ethyl acetate to give 2 g. of **10**, m.p. 195-196°.

The nmr (deuteriochloroform) for **10** showed a doublet δ 7.5 (1H) for the H₉ proton, a multiplet δ 7.67-8.0 (3H) for the H_{5,6,7} protons, a doublet δ 8.17 (1H) for the H₈ proton, a singlet δ 8.52 (1H) for the H₁ proton, a multiplet at δ 9.95 (1H) for the H₇ proton, and a singlet δ 10.5 ppm (1H) for the aldehyde proton.

The nmr (1,2,3-trichloropropane) for **12** showed a doublet 5.5 (1H) for H₈, a multiplet δ 6.15 (1H) for H₅, a multiplet δ 6.85 (3H) for H_{4,6,7}, a singlet δ 7.78 (1H) for H₃, a singlet at δ 10.6 (1H) for the aldehyde proton, and a broad singlet δ 15.8 ppm (1H) for the OH.

Anal. Calcd. for **10**, C₁₄H₈O₃: C, 75.0; H, 3.6. Found: C, 75.2; H, 3.7.

Anal. Calcd. for **12**, C₁₄H₈O₃: C, 75.0; H, 3.6. Found: C, 75.3; H, 3.8.

9-Hydroxy-1-phenalenone.

A mixture of 1 g. of the aldehyde (**12**), 0.2 g. of tris(triphenylphosphine) rhodium (I) chloride, and 15 ml. of phenylacetonitrile was refluxed for 5 hours and filtered hot. The filtrate was cooled and extracted with three 25 ml. portions of concentrated hydro-

chloric acid. Dilution of the acid extracts with water afforded the solid 9-hydroxy-1-phenalenone, which was recrystallized from alcohol to give 0.51 g. of product, m.p. 197-198° (reported m.p. 199-200° (3)). The UV absorption spectrum was identical with the published values.

Anal. Calcd. for C₁₃H₈O₂: C, 79.6; H, 4.1. Found: C, 79.7; H, 4.0.

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