

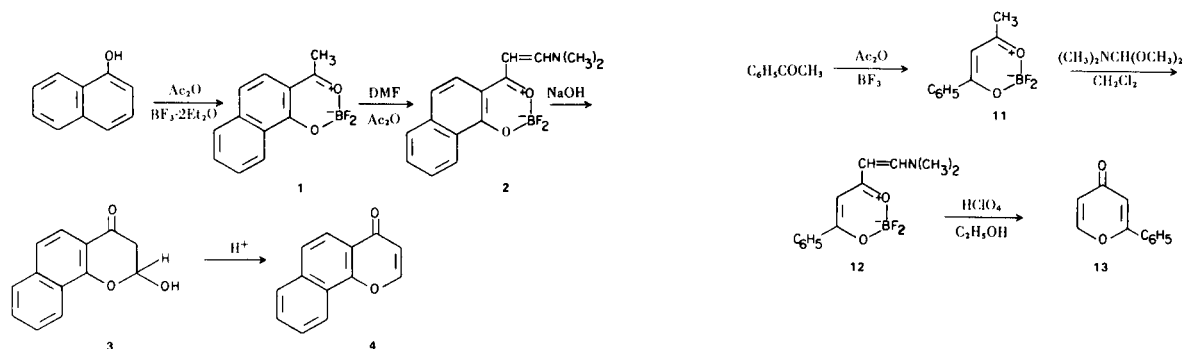
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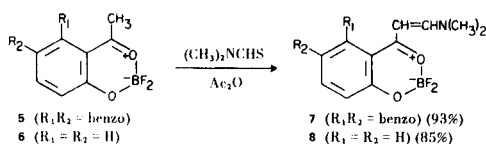
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A general procedure for the preparation of chromones from the boron difluoride complex of *o*-hydroxyaryl methyl ketones is described. One of the best methods used for the preparation of chromones and benzochromones is the treatment of *o*-hydroxyaryl methyl ketones with the dimethylacetal of dimethylformamide followed by treatment with sulfuric acid (1). We previously had shown (2) that benzochromone **4** was prepared in reasonable yield by the following reaction sequence.

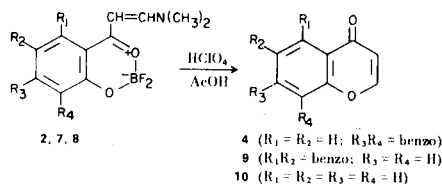
J. Heterocyclic Chem., **16**, 369 (1979).



The procedure did not give satisfactory yields of chromone (**10**) or benzo[*f*]chromone (**9**) and therefore cannot be considered to be a general synthetic method. We now report the experimental conditions for using our method to prepare **9** and **10** in good yield and the elimination of a step in the reaction sequence. The procedure used to convert **1** to **2** gave very poor yields with the boron difluoride complexes **5** and **6**. A number of other methods were investigated, and the most satisfactory was *N,N*-dimethylthioformamide in acetic anhydride.



The conversion of **2**, **7**, and **8** to chromones has been simplified by treating the complexes with 35% perchloric acid in acetic acid or alcohol to give the chromones directly in high yields.



The general method has been extended to include the preparation of 2-substituted-4-pyrones as illustrated by the synthesis of 2-phenyl-4*H*-pyran-4-one (**13**).

EXPERIMENTAL

Preparation of Methyl Boron Difluoride Complexes.

The complexes **1** (**5**), **5** (**3**), and **6** (**4**) were prepared by the published procedures. Compound **11** was prepared as follows. A mixture of acetophenone (25 g., 0.208 mole) and acetic anhydride (42.5 g., 0.416 mole) was cooled to 5-10° while passing boron trifluoride through the solution until it solidified. After standing 1 hour, the solid was collected and washed with ether. A second crop was obtained from the filtrate. The combined yield of **11** was 40 g. (92%), m.p. 147-150° [lit. (**4**) 156-157°].

Preparation of Dimethylaminovinyl Boron Difluoride Complexes (**2**, **7**, **8**, **12**).

Compound **2** was prepared in 81% yield by the method described previously (2). Compound **7** was prepared as follows. A mixture of **5** (0.05 mole), *N,N*-dimethylthioformamide (7.5 ml.), and acetic anhydride (10 ml.) was heated on a steam bath for 3 hours. The solid was collected and washed with acetic acid to yield **7** (13.1 g., 93%), m.p. 261-263° [lit. (**3**) 265-266°].

Compound **8**.

This compound was prepared from **6** (0.05 mole) by the procedure described for the preparation of **7**, m.p. 250-251° (from acetic acid).

Anal. Calcd. for $C_{11}H_{12}BF_2NO$: C, 55.3; H, 5.1; N, 5.9. Found: C, 55.5; H, 5.3; N, 5.9.

Compound **12**.

This compound was prepared by heating (60°) a suspension of **11** (0.149 mole) in 50 ml. of DMF and slowly adding *N,N*-dimethylthioformamide dimethylacetal (23.8 g., 0.2 mole) with stirring. The temperature was raised to 95° for 1.5 hours and the solid that had separated was collected and washed with ether to give **12** (28.3 g., 72%), m.p. 215-216°.

Anal. Calcd. for $C_{13}H_{14}BF_2NO_2$: C, 58.9; H, 5.3; N, 5.3.

Found: C, 58.9; H, 5.6; N, 5.3.

General Procedure for the Preparation of Chromones **4**, **9**, and **10** and Pyrone **13**.

A mixture of 0.02 mole of **2**, **7**, or **8**, 25 ml. of acetic acid, 6 ml. of 70% perchloric acid, and 6 ml. of water was refluxed for 2 hours. The solution was diluted with 100 ml. of water and the solid was collected and dried in a desiccator over phosphorus pentoxide.

Compound **4**.

This compound was recrystallized from heptane, yield 3.2 g. (83%), m.p. 121-122° [lit. (2) 120-121°].

Compound **9**.

This compound was recrystallized from hexane, yield 3.5 g. (90%), m.p. 99-100° [lit. (2) 100-101°].

Compound **10**.

This compound was recrystallized from petroleum ether, yield 2.8 g. (96%), m.p. 57-58° [lit. (1) 59°].

Pyrone **13**.

This compound was prepared by refluxing a suspension of **12** (3 g., 0.0113 mole) in alcohol (100 ml.), water (5 ml.), and 70% perchloric acid (5 ml.) until a clear solution was obtained (2 hours). The alcohol was removed on a rotary evaporator and the residue was cooled. The solid was collected, recrystallized from aqueous alcohol, and dried over phosphorus pentoxide, yield 1.55 g. (80%), m.p. 101-103° [lit. (5) 103-104°].

Anal. Calcd. for C₁₁H₈O₂: C, 76.9; H, 5.0. Found: C, 76.9; H, 4.7.

REFERENCES AND NOTES

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