

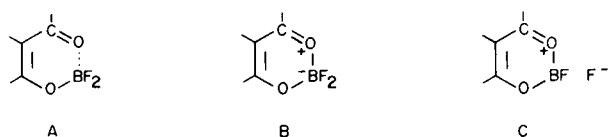
The Reactions of 2,2-Difluoro-4-methylnaphtho[1,2-*e*]-1,3,2-dioxaborin and Its [2,1-*e*] Isomer with Carbonyl Compounds and with Aniline

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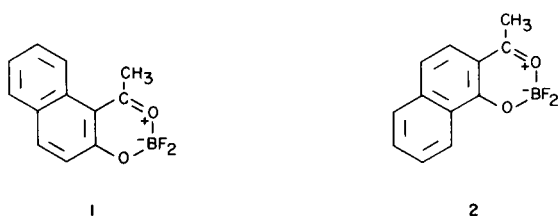
2,2-Difluoro-4-methylnaphtho[1,2-*e*]-1,3,2-dioxaborin (**1**) and its [2,1-*e*] isomer (**2**) react with equimolecular quantities of carbonyl compounds, giving colored ethylenic derivatives. With aniline, **1** and **2** give the corresponding oxazaborins **21** and **22**. The structures of **1** and **2** are discussed.

It has been known for many years that the enol form of β -diketones and *o*-hydroxyaryl ketones and aldehydes react with boron trifluoride to give complexes which contain the BF_2 moiety. Various structures, such as A, B, and C, have been proposed for these compounds, but structure B is considered to best represent the complex (1). Although many compounds of this type have been



described, their chemistry has not been fully explored. The present paper describes some reactions which have been carried out using certain of these complexes.

The reaction of 2-naphthol with boron trifluoride acetic acid gives compound **1**, and 1-naphthol with acetic anhydride in the presence of boron trifluoride etherate yields **2**, which had been prepared previously by Cram. (1).



Compound **2** hydrolyzes in boiling alcohol to give 2-acetyl-1-naphthol, while **1** is stable and is hydrolyzed only by base. The nmr spectra (2) of **1** and **2** show the protons

of the methyl group at an unusually low field (6.85 τ and 6.9 τ for **1** and **2**, respectively, in acetone- d_6) compared to the methyl group of a ketone or a methyl group attached to an aromatic ring. This effect may be ascribed to the positive charge on the oxygen atom. The values for the methyl groups of some other compounds are given in Table I for comparison with **1** and **2**.

The methyl groups of **1** and **2** were found to react with electrophilic compounds. Therefore **1** was allowed to react with dimethylformamide, anisaldehyde, diethylaminoacrolein, 3-formyl-4*H*-flavene, 4-dimethylaminobenzal-

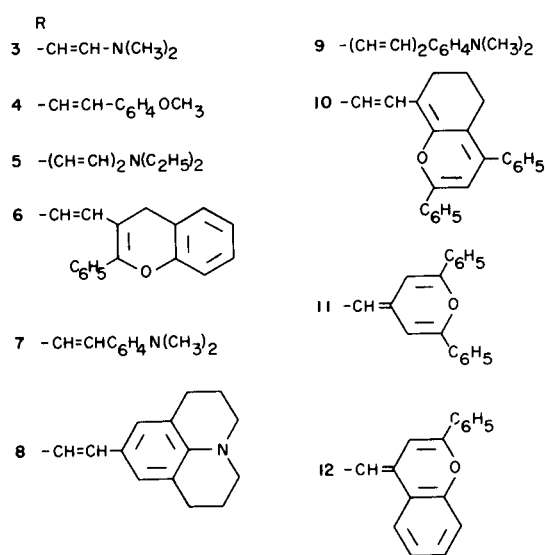
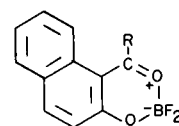
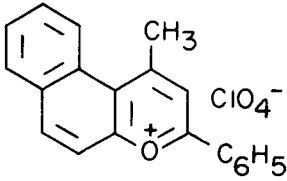
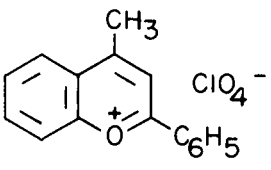
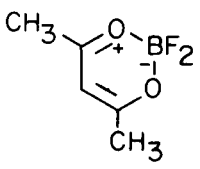
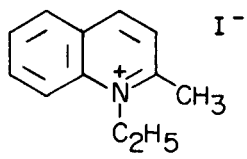
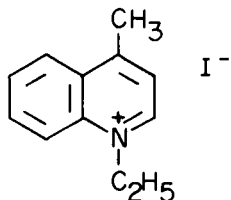


TABLE I
 τ Values for Methyl Groups

Compound	τ Value	Solvent
1	6.93 6.85	CF ₃ CO ₂ H acetone-d ₆
2	7.07 6.90	CF ₃ CO ₂ H acetone-d ₆
1-acetyl-2-naphthol	7.28 7.3	acetone-d ₆ CDCl ₃
2-acetyl-1-naphthol	7.52	acetone-d ₆
	6.42	CF ₃ CO ₂ H
	6.72	CF ₃ CO ₂ H
	7.72 (a)	CDCl ₃
	7.19	CF ₃ CO ₂ H
	7.33 6.87	CF ₃ CO ₂ H acetone-d ₆

(a) A. Trestianu, H. Niculescu-Mojewska, I. Bally, A. Barabas and A. T. Balaban, *Tetrahedron*, 24, 2499 (1968).

TABLE II
Absorption Spectra in Acetonitrile

Compound	λ max $m\mu$ ($\epsilon \times 10^{-3}$)				
1	205 (23.5) 218 (49.8)	\sim 242 282 (6.0)	350 (9.9)	\sim 390-400	
2	215 (35.9)	264 (56.3) 298 (14.5)	310 (16.8)	410 (4.2)	
3	245 (23.8) 273 (6.4)	315 (6.4)	340 (5.2) 412 (31.2)	428 (27.6)	
4	224 (43.6)		374 (12.4)	470 (21.0)	
5	240 (13.5)	315 (6.4)	345 (6.4)	484 (54.7)	512 (57.8)
6	238 (29.0)		340 (14.2)	\sim 380 (7.2) \sim 520 (34.0)	540 (72.0)
7	252 (10.8)	275 (10.0)	342 (8.4)		570 (72.0)
8			350 (6.9)		610 (63.1)
9	224 (30.0)	305 (7.3)	360 (9.8)	425 (9.2)	620 (55.5)
10	265 (16.4)	\sim 296 (8.7) \sim 341 (11.0)	415 (5.5)	660 (28.7)	704 (27.9)
11	247 (30.7)	266 (19.8)			526 (66.0)
12	235 (32.3)		339 (16.0)		538 (56.5)
13	\sim 253 (20.5)	269 (21.0) 278 (27.2)	378 (65.0)	465 (30.0)	
14	265 (19.2)	327 (8.0)	408 (29.5)	478 (35.5)	
15	227(17.0) 265(12.9)	329 (9.3)			569 (89.0)
16	278 (46.4)	370 (13.6)	410 (11.8)		520 (66.4)
17(a)	268	357	431 456		670 708

(a) The spectrum of the compound was determined in methyl sulfoxide. The extinction coefficients are not given because of incomplete solution.

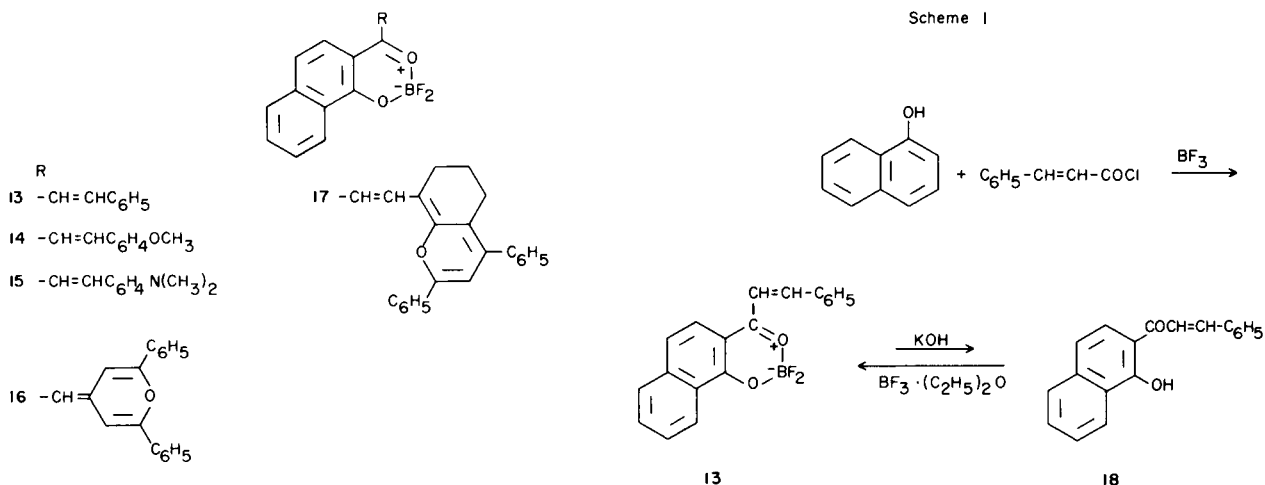
hyde, 5-formyljulolidine, dimethylaminocinnamaldehyde, 8-ethoxymethylene-2,4-diphenyl-5,6,7,8-tetrahydrobenzo[*b*]pyrylium perchlorate, 2,6-diphenyl-4-pyrone, and flavone to give compounds **3-12**, respectively. In most cases these compounds were prepared by heating equimolecular quantities of the components in acetic anhydride. Compounds **3-12** are colored and their

electronic absorption spectra are recorded in Table II.

The isomeric compound **2** reacts in a similar manner with benzaldehyde, anisaldehyde, *p*-dimethylaminobenzaldehyde, 2,6-diphenyl-4-pyrone, and 8-ethoxymethylene-2,4-diphenyl-5,6,7,8-tetrahydrobenzo[*b*]pyrylium perchlorate to give compounds **13-17**. The absorption spectra of these compounds are recorded in Table II.

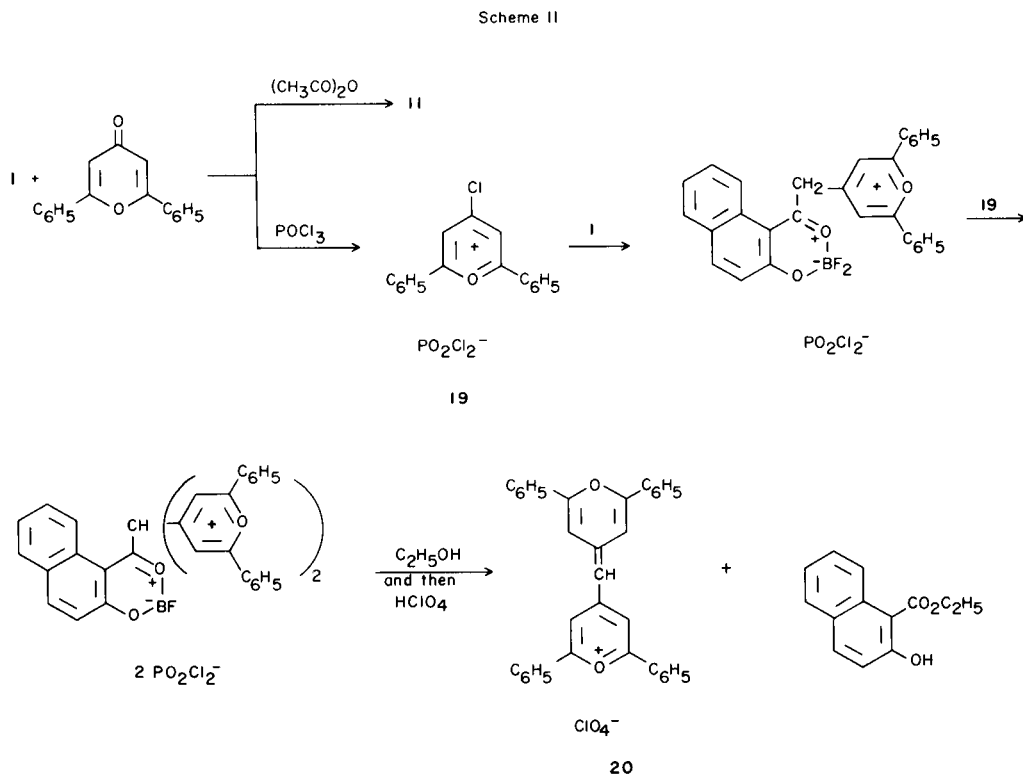
TABLE III
 Physical Properties and Methods of Preparation

Compound	M.p. °C	Empirical formula	Anal. Calcd./Found				Method of preparation	Yield %	Solvent of recrystallization
			C	H	N	F			
1	180-181	C ₁₂ H ₉ BF ₂ O ₂	61.6 61.3	3.9 4.2			See Expt.	77	butyl alcohol
2	247-248	C ₁₂ H ₉ BF ₂ O ₂	61.6 61.4	3.9 4.0			See Expt.	83	acetonitrile
3	265-266	C ₁₅ H ₁₄ BF ₂ NO ₂	62.3 62.1	4.9 4.8	4.8 4.8		A (15 min.)	48	acetonitrile
4	214-216	C ₂₀ H ₁₅ BF ₂ O ₃	68.2 67.9	4.3 4.4		10.8 10.7	B	44	acetonitrile
5	209-210	C ₁₉ H ₂₀ BF ₂ NO ₂	66.5 66.7	5.9 6.0	4.1 3.9		A (2 hr.)	24	acetic acid
6	214-215	C ₂₈ H ₁₉ BF ₂ O ₃	74.4 74.1	4.2 4.6		8.4 8.3	C	12	ethyl alcohol
7	199-200	C ₂₁ H ₁₈ BF ₂ NO ₂	69.1 69.1	5.0 5.2		10.4 10.1	A (2 hr.)	74	acetonitrile
8	224-225	C ₂₅ H ₂₂ BF ₂ NO ₂	72.0 72.1	5.3 5.5		9.1 8.9	A (2 hr.)	79	acetonitrile
9	229-230	C ₂₃ H ₂₀ BF ₂ NO ₂	70.6 70.9	5.2 5.4	3.6 3.4		A (2 hr.)	73	acetonitrile
10	278-279	C ₃₄ H ₂₅ BF ₂ O ₃	77.0 77.1	4.8 4.7		7.2 6.8	D	89	acetonitrile
11	304-306	C ₂₉ H ₁₉ BF ₂ O ₃	75.0 74.8	4.1 4.3		8.2 7.9	A (1 hr.)	69	acetonitrile
12	259-260	C ₂₇ H ₁₇ BF ₂ O ₃	74.0 73.8	3.9 4.6		8.7 8.6	A (12 hr.)	83	acetonitrile
13	269-270	C ₁₉ H ₁₃ BF ₂ O ₂	70.8 70.8	4.1 3.7		11.8 11.6	B	73	acetonitrile
14	294-295	C ₂₀ H ₁₅ BF ₂ O ₃	68.2 68.5	4.3 4.4		10.8 10.8	C	40	acetonitrile
15	290-291	C ₂₁ H ₁₈ BF ₂ NO ₂	69.0 68.9	5.0 5.1		10.4 10.4	A (2 hr.)	86	acetonitrile
16	345-347	C ₂₉ H ₁₉ BF ₂ O ₃	75.0 74.9	4.1 4.4		8.2 8.2	A (3 hr.)	79	dimethylformamide
17	> 380	C ₃₄ H ₂₅ BF ₂ O ₃	77.0 77.3	4.8 4.8		7.2 7.0	D	92	insoluble
18	126-127	C ₁₉ H ₁₄ O ₂	P. Pfeiffer, E. Kalekbrenner, W. Kunze and K. Levin, <i>J. Prakt. Chem.</i> , 119, 109 (1928).						
20	328-330	C ₃₅ H ₂₅ ClO ₆	72.8 72.8	4.4 4.5	(Cl) 6.2 6.4		See Expt.	85	acetonitrile
21	190-191	C ₁₈ H ₁₄ BF ₂ NO	69.9 69.8	4.6 4.7		12.3 12.3	See Expt.	68	acetic acid
22	269-270	C ₁₈ H ₁₄ BF ₂ NO	69.9 69.5	4.6 4.5		12.3 12.5	See Expt.	83	acetonitrile

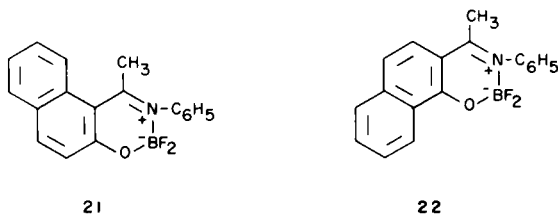


As a proof of structure for the reaction products of 1 and 2 with carbonyl compounds, several of the products were hydrolyzed by base to give the hydroxy ketone which was in turn treated with boron trifluoride etherate to regenerate the complex. Several of the complexes were also prepared from naphthol and an unsaturated acid chloride. Examples of these reactions are shown in Scheme I.

The reaction of 1 with 2,6-diphenyl-4-pyrone in phosphoryl chloride in place of acetic anhydride gave the dye 20, rather than 11, and a possible reaction scheme is shown in Scheme II.



Aniline reacts with **1** and **2** to give compounds which were arbitrarily assigned structures **21** and **22**, respectively. The nmr and mass spectra of these compounds did not give information which allows us to distinguish between these structures and the alternate possibility in which the



other oxygen atom has been displaced. Hydrolysis of **21** and **22** with base gave the corresponding *o*-hydroxyketones. Although we do not consider this to be proof for structures **21** and **22**, it is consistent with them. Attempts to prepare **21** by the reaction of 1-acetyl-2-naphthol with aniline to give the anil and subsequent treatment with boron trifluoride were unsuccessful. The methyl group of **21** and **22** is less reactive than that of **1** and **2**, since the former compounds did not react with aldehydes in acetic anhydride. The τ values for the methyl groups are 7.34 for **21** and 7.39 for **22** in acetone- d_6 .

The dye **5** was examined by electrophoresis, using acetonitrile as a solvent and ammonium perchlorate as a supporting electrolyte, to see if this type of compound is ionized (see structure C). The compound remained at the reference point and is assumed to be undissociated. Conductance measurements were also made on **5**, but again the results indicated an undissociated species. On the basis of these data, it appears that the heterocyclic ring of **5** is represented by structure B.

EXPERIMENTAL

The physical properties and method of preparation for the compounds are recorded in Table III.

2,2-Difluoro-4-methylnaphtho[1,2-*e*]-1,3,2-dioxaborin (**1**).

A mixture of 10 g. of β -naphthol and 15 ml. of boron trifluoride acetic acid was heated on a steam bath for 1 hour, cooled, and the solid was collected and recrystallized.

2,2-Difluoro-4-methylnaphtho[2,1-*e*]-1,3,2-dioxaborin (**2**).

A mixture of 10 g. of α -naphthol, 25 ml. of acetic anhydride, and 15 ml. of boron trifluoride etherate was heated on the steam bath for 1 hour, cooled, and the solid was collected. The procedure used for the preparation of **1** was unsuccessful with α -naphthol.

General Procedure A.

A mixture of 0.1 mole of **1** or **2** and 0.11 mole of the carbonyl compound in 50 ml. of acetic anhydride was heated on the steam bath for the time specified in Table III. If the product separated when the reaction mixture was chilled, the solid was collected and recrystallized; otherwise, the acetic anhydride was decomposed with water and the precipitated product was then recrystallized.

General Procedure B.

A mixture of 0.02 mole of **1** or **2** and 20 ml. of aldehyde was heated on the steam bath for 15 hours. The reaction mixture was chilled, and the solid was collected and washed with ethyl ether.

General Procedure C.

A mixture of 0.01 mole of **1** or **2**, 0.015 mole of the aldehyde, and 25 ml. of 1,2,3-trichloropropane was heated at reflux for 2 hours, cooled, and the solid was collected.

Procedure D.

A mixture of 2.34 g. of **1** or **2**, 4.42 g. of 8-ethoxymethylene-2,4-diphenyl-5,6,7,8-tetrahydrobenzo[*b*]pyrylium perchlorate, 3 ml. of diisopropylethylamine, and 100 ml. of acetonitrile was heated at reflux for 1 hour, cooled, and the precipitate was collected.

2,2-Difluoro-4-methyl-3-phenylnaphtho[1,2-*e*]oxazaborin (**21**).

A solution of 2.34 g. of **1** and 1 ml. of aniline in 15 ml. of toluene was heated on a steam bath for 3 hours and filtered hot. The filtrate was chilled and the solid was collected.

2,2-Difluoro-4-methyl-3-phenylnaphtho[2,1-*e*]-1,3,2-oxazaborin (**22**).

A mixture of 4.7 g. of **2**, 2 ml. of aniline, and 60 ml. of acetonitrile was allowed to react by the procedure described for the preparation of **21**.

2-Cinnamoyl-1-naphthol (**18**).

A mixture of 33.2 g. of cinnamoyl chloride, 28.8 g. of 1-naphthol, and 200 ml. of boron trifluoride etherate was heated on a steam bath for 4 hours, cooled, and the red crystals were collected and recrystallized from acetonitrile to give 35 g. of 2,2-difluoro-4-styrylnaphtho[2,1-*e*]-1,3,2-dioxaborin (**13**) which had an identical m.p. and infrared absorption curve with a sample prepared by Procedure B.

A mixture of 2 g. of **13** and 25 ml. of 5% methanolic potassium hydroxide was stirred for several minutes and poured into aqueous acetic acid. The solid was collected and recrystallized from ethoxyethanol to give 1.2 g. of **18**.

A mixture of 2 g. of **18** and 10 ml. of boron trifluoride etherate was heated on the steam bath, chilled, and 2.1 g. of **13** was collected.

4-(2,6-Diphenyl-4-pyranylidene)methyl-2,6-diphenylpyrylium perchlorate (**20**).

A mixture of 2.4 g. of **1**, 5 g. of 2,6-diphenyl-4-pyrone, and 8 ml. of phosphoryl chloride was heated for 2 hours on the steam bath, poured into methanol, and 5 ml. of 70% perchloric acid was added to the mixture. The solid was collected and recrystallized from acetonitrile to yield **20**. The product displayed an ultraviolet and infrared absorption curve identical with a sample prepared by the reaction of 2,6-diphenyl-4-pyrone and 4-methyl-2,6-diphenylpyrylium perchlorate.

Acknowledgment.

We are indebted to T. H. Regan and R. L. Young for the determination and interpretation of the nmr spectra.

(1) D. S. Cram, *J. Am. Chem. Soc.*, 71, 3953 (1949).

(2) The nmr spectra were measured at 60 mhz on a Varian A-60 spectrometer with tetramethylsilane as an internal standard.

REFERENCES

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