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On the Formation and Solvolysis of 4-Aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines

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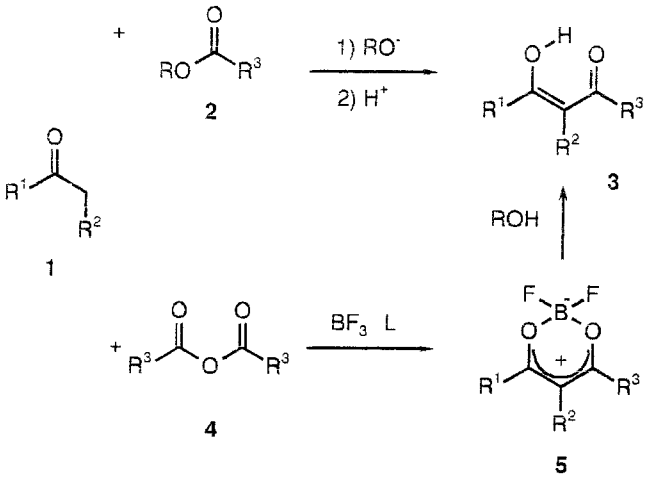
ABSTRACT

The condensation of aryl methyl ketones **6** *with acetic anhydride* **4a** *in the presence of the boron trifluoride-acetic acid adduct* **7** *gives rise to the formation of 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines* **8** *in satisfactory yields. The stable 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines* **8** *can be transformed by hydrolysis into the corresponding aroylacetones* **9**. *The reaction was optimized so as to avoid the formation of by-products, such as 2,4-diaryl-6-methylpyrylium tetrafluoroborates* **11** *or self-condensation products.* © *1997 John Wiley & Sons, Inc.*

1,3-Dicarbonyl compounds **3** are important synthons for the preparation of different types of organic compounds, especially heterocyclic compounds [1]. Their synthesis is usually performed by a Claisen-type reaction consisting in the condensation of a methyl or methylene substituted ketone **1** with an alkyl or aryl carboxylate **2** in the presence of a strong base, such as a metal alkoxide or a metal hydride, under water-free conditions [2]. Therefore, the Claisen condensation is inapplicable under certain circumstances, e.g., by starting with educts bearing base-sensitive groups. With such educts, an alternative synthesis elaborated by H. Meerwein et al. [3] is more useful. It consists in the condensation of **1** with a carboxylic acid anhydride **4** in the presence of boron trifluoride. This reaction takes place via boron- and fluorine-containing intermediates, their structures having been elucidated as 2,2-difluoro-1,3,2-(2H)-dioxaborines **5** by other authors some time later [4] (Scheme 1).

A detailed investigation of the Meerwein synthesis of 1,3-dicarbonyl compounds **3** reveals that the 2,2-difluoro-1,3,2-(2H)-dioxaborines **5** are not the only products formed in the course of this reaction.



SCHEME 1

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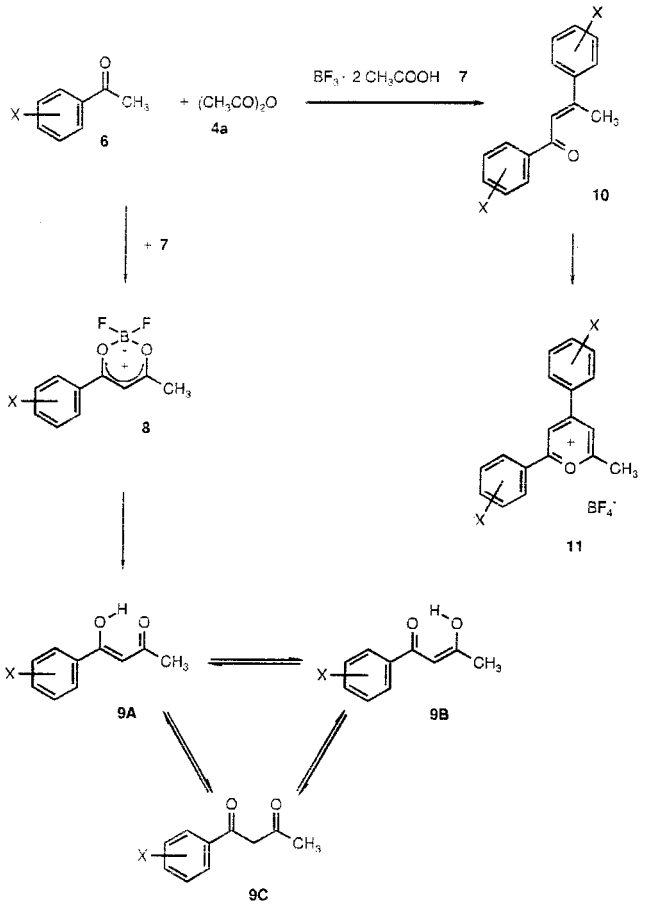

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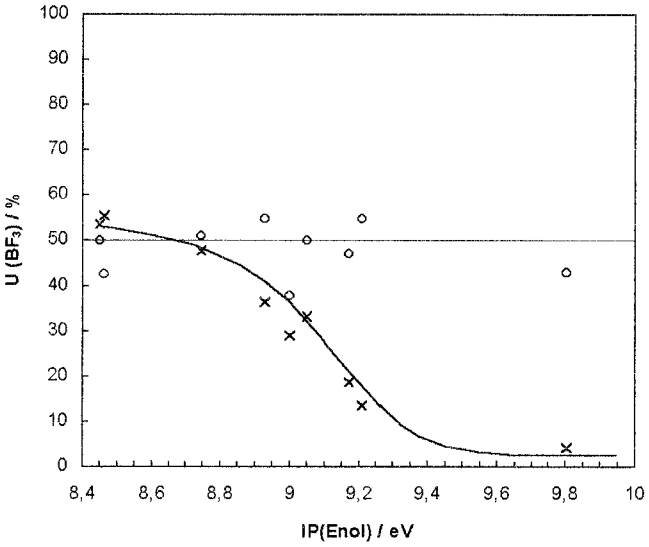


FIGURE 1. Plot of the turnover to **8** ○ and **11** × respectively, vs. calculated (PM3) ionization potentials of the corresponding enols of **6**. The reaction extent was determined by ^{1}H NMR spectroscopy and is related to the boron trifluoride used. For details, see text and Table 1.

Besides 2.2-difluoro-1,3,2-(2H)-dioxaborines **5**, the formation of self-condensation products of the starting acid anhydrides **4** has been observed, especially if gaseous boron trifluoride were used. Moreover, in the course of the condensation of acetophenones **6** with acetic anhydride **4a** in the presence of boron trifluoride, the formation of pyrylium-tetrafluoroborates has been observed. These pyrylium salts can even be the main products of the reaction, especially if acetophenones having electron donating substituents are used [5]. Hence, the Meerwein synthesis for 1,3-dicarbonyl compounds **3** loses some of its preparative value, unless it is possible to reduce or to avoid the formation of the by-products mentioned herein.

For the purpose of eliminating the reported restrictions of the Meerwein synthesis, we have studied the condensation of several differently substituted acetophenones **6** with acetic anhydride **4a** in the presence of boron trifluoride—acetic acid—complex **7** in more detail. The reaction results were monitored by means of ^{1}H NMR spectroscopy by determining the methyl signal intensities of the educts and products, in dependence of the substitution pattern of the educts **6** and of the reaction conditions applied. The results obtained give rise to a simple and by-product–free preparative method for aroylacetones **9** as well as for their 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborine precursors **8** (Scheme 2).

The results of the ^{1}H NMR spectroscopic measurements of the condensation reaction of substituted acetophenones **6** with acetic anhydride **4a** and boron trifluoride—acetic acid—complex **7** are listed in Table 1 (for details see Experimental).

These data reveal that the formation of the corresponding 2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** is nearly independent of the kind of substituent *X* in the starting acetophenones **6**. However, the yields of the 4,6-diaryl-2-methylpyrylium tetrafluorobonates **11** formed are strongly dependent on the substituent *X* in the aryl moiety of the acetophenone **6** used. They can be correlated, as shown in Figure 1, with the calculated ionization potentials of the enol forms of the corresponding acetophenones **6** much better than with the Hammet σ-constants of the substituents *X* due to the fact that the enol derivatives are the reactive species that primarily react with the acylating reagent. When acetophenones **6** with electron-withdrawing substituents, *X*, were used, only small amounts of the starting materials were transformed into the corresponding pyrylium salts **11**. On the other hand, respectable amounts of pyrylium salts **11** were formed if acetophenones **6** with electron donor substituents were

TABLE 1 Results of the ^{1}H NMR Spectroscopic Investigations on the Condensation Pathway of Substituted Acetophenones **6** with Acetic Anhydride **4a** in the Presence of Boron Trifluoride—Acetic Acid—Complex **7**

			Composition of the Reaction Mixture in %			*Reaction Extent[a] in %, Related to BF_3*	
X	σ_p *[13]*	$iP_{(Enol)}$*/eV (PM3)*	**8**	**11**	**6**	**8**	**11**
4-OCH_3	−0.27	8.743	41.6	19.4	39.0	51.1	47.7
4-CH_3	−0.17	8.931	42.9	14.2	42.9	55.0	36.3
4-SCH_3	±0.00	8.463	35.7	23.2	41.0	42.6	55.4
4-SC_2H_5	—	8.450	41.5	22.2	36.3	49.9	53.5
H	±0.00	9.050	38.5	12.8	48.7	50.1	33.3
4-F	+0.06	9.173	34.1	6.8	59.1	47.0	18.7
4-Cl	+0.23	9.001	28.5	11.0	60.5	37.8	29.1
4-Br	+0.23	9.210	41.2	10.0	48.7	55.0	13.5
4-NO_2	+0.78	9.803	29.6	1.4	69.0	42.9	4.1

[a]The reaction extend U calculated in respect to the ratio of **7** used as follows ([**j**] means the concentration of the component **j**):

for compound **8**:

$$U([\mathbf{8}]/[BF_3]) = \frac{[\mathbf{8}]}{[\mathbf{8}] + 2[\mathbf{11}]} \Big/ 0.68$$

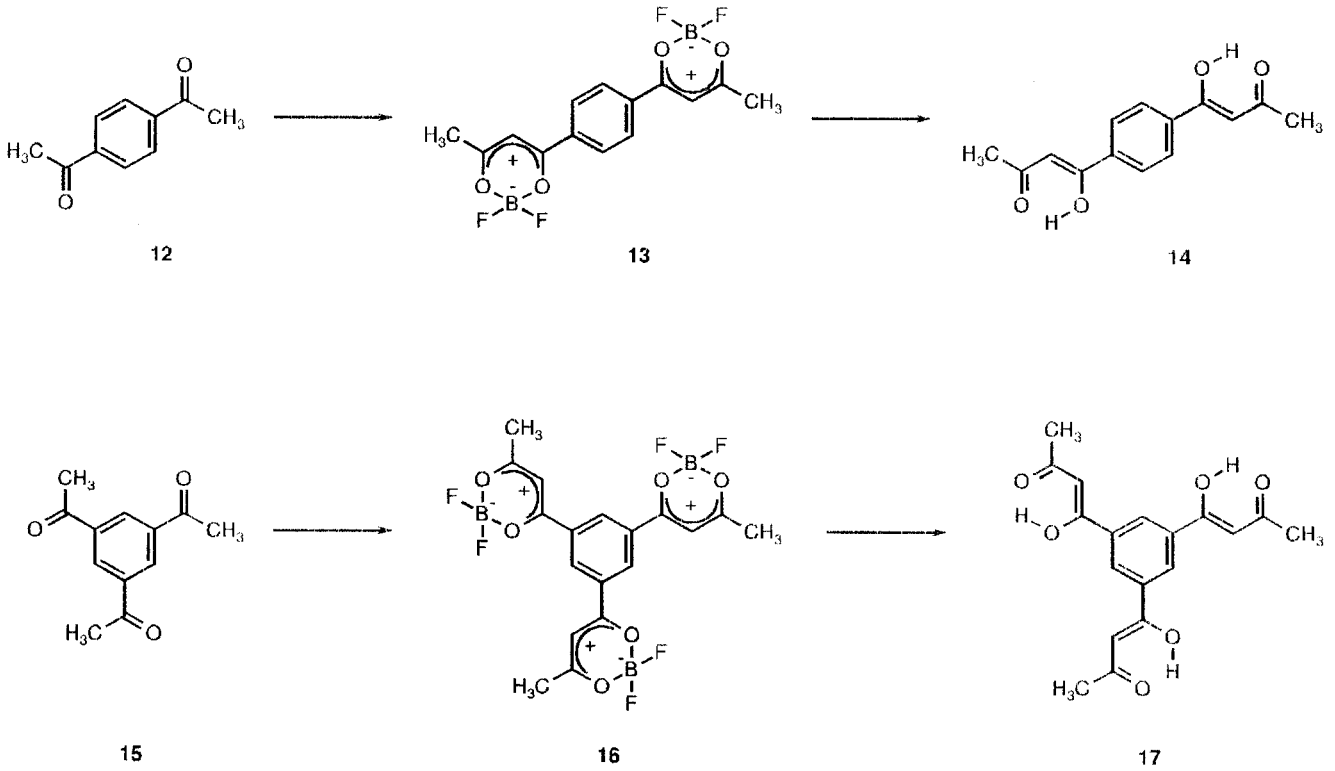
for compound **11**:

$$U([\mathbf{11}]/[BF_3]) = \frac{2[\mathbf{11}]}{[\mathbf{8}] + 2[\mathbf{11}]} \Big/ 0.68$$

TABLE 2 Yields and Melting Points of 2,2-Difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** and Aroylacetones **9**

X	*Nr.*	*Yield [%]*	*Mp [°C] (Lit.)*	*Nr.*	*Yield [%]*	*Mp [°C] (Lit.)*
4-H	**8a**	75	160–161[a] (158–159 [5])	**9a**	88	56–57 (60–61 [14])
4-CH_3	**8b**	64	172–173[a]	**9b**	63	19–21
4-OCH_3	**8c**	73	170[a]	**9c**	88	53–54 (54.5 [15])
4-SCH_3	**8d**	77	177–179[b]	**9d**	99	109–110
4-SC_2H_5	**8e**	56	129[c]	**9e**	79	76–77
4-$N(CH_3)_2$	**8f**	33	226–227[b]	**9f**	93	113 (114–118 [16])
4-F	**8g**	71	183[a]	**9g**	82	47 (48–49 [17])
4-Cl	**8h**	79	227–228[a] (226–228 [5])	**9h**	87	70–71 (72–73 [18])
4-Br	**8i**	86	223–226[b]	**9i**	92	91–92 (92.5 [19])
4-I	**8j**	69	199–205[a]	**9j**	93	117–118
4-NO_2	**8k**	50	219 (dec.)[b]	**9k**	74	116–117 (112–112.8 [20])
3,4-$(OCH_3)_2$	**8l**	45	158–159[b]	**9l**	79	71 (69–71 [21])
2,3-Benzo	**8m**	48	158[b]			
3,4-Benzo	**8n**	89	191–192[b]	**9n**	92	78–79 (81.5–82.5 [22])
4-$N(CH_3)_3^+$	**8o**	86	230–232[b] (dec.)	**9o**	61	180–183
	13	88	293–300[d]	**14**	87	145–146 (184 [23])
	16	49	>360	**17**	62	159–161

Compounds **8** were recrystallized from [a]ethyl acetate, [b]acetic acid, [c]toluene, and [d]mixture of acetic acid—acetic anhydride.

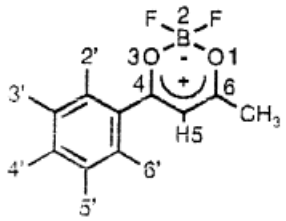


SCHEME 3

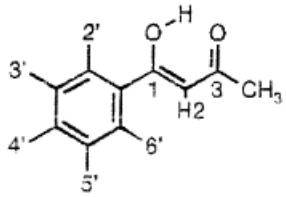
used. However, even by using acetophenones with strong electron-donating substituents, *X*, the yields of the corresponding pyrylium salts **11** do not exceed essentially more than 50%, relative to the boron trifluoride—acetic acid—complex **7** used.

At first glance, our findings seem to indicate that the preparation of 2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8**, as precursors of the aroyl acetones **9**, by means of the boron trifluoride-mediated condensation of an acetophenone with acetic anhydride is attractive only if acetophenones **6** with strong electron-accepting substituents, *X*, are used. Otherwise, the formation of considerable amounts of the corresponding 4,6-diaryl-2-methylpyrylium tetrafluoroborates **11** occurs. The formation of these diaryl-substituted pyrylium salts **11** takes place, however, as proposed previously by Durden and Crosby [5], via the corresponding dypnones **10**, which are formed from the starting acetophenone **6** by a self-condensation reaction initiated by the boron trifluoride reagent **7** in yields that rise with increasing reaction temperatures and increasing reaction times. Consequently, for lowering the amount of dypnone **10** formed, a reduction of the concentration of the acetophenone **6** is required. This can be accomplished by a dropwise addition of the required acetophenone **6** during the reaction. By this mode of operation, the formation of dypnones **10** and, consequently, the formation of pyrylium salts **11** derived from them is depressed. Indeed, maintenance of reaction temperatures between 40 and 50 °C and addition of the appropriate acetophenones **6** into the mixture of the other reaction components during a period of 6–8 hours provide the best conditions for obtaining optimal yields of the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8**. For obtaining nearly a complete turnover of the acetophenone **6** into the corresponding 2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborine **8**, a molar acetophenone/boron trifluoride ratio of 1:2 is recommended. Under these conditions, high yields of 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** that are free of pyrylium salts **11** have been obtained. In most of the examples, the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** crystallized during the addition of the acetophenone **6**. At the end of the acetophenone addition, the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** formed can be isolated by suction filtration. The 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** prepared by the procedure just described are crystalline compounds that can be handled in air but with exclusion of moisture, without decomposition. Toward solvents contains a hydroxyl group, such as, water or alcohols, the dioxa-

TABLE 3 ^{1}H NMR Chemical Shifts (in ppm, Relative to Hexamethyl Disiloxane $\delta = 0.04$ ppm) and Coupling Constants (in Hz) of the 2,2-Difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** (Measured in CD_3NO_2), and **8m** as well as of the Aroylacetones **9e**, **9o**, **14**, and **17** (Measured in $CDCl_3$)



8



9

Nr.	*6-CH_3*	*5-CH*	*4-Ar Assignments*	*Coupling Constants /Hz*	*Additional Signals Assignments*
8a	2.42	6.83	8.08 (d, 2H, H2′, H6′) 7.57 (t, 2H, H3′, H5′) 7.73 (t, 1H, H4′)	$J_{2'3'} = J_{5'6'} = 7.46$ $J_{3'4'} = J_{4'5'} = 7.42$	
8b	2.41	6.78	7.97 (d, 2H, H2′, H6′) 7.37 (d, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 8.22$	2.39 (s, 3H, -Ph-CH_3)
8c	2.36	6.72	8.09 (d, 2H, H2′, H6′) 7.08 (d, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 9.10$	3.91 (s, 3H, OCH_3)
8d	2.38	6.77	8.00 (d, 2H, H2′, H6′) 7.39 (d, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 8.61$	2.55 (s, 3H, -SCH_3)
8e	2.38	6.75	7.97 (d, 2H, H2′, H6′) 7.38 (d, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 8.55$	1.35 (t, 3H, CH_2-CH_3) 3.08 (q, 2H, -CH_2-S)
8f	2.25	6.53	7.96 (d, 2H, H2′, H6′) 6.79 (d, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 9.34$	3.15 (s, 6H, -N(CH_3)$_2$)
8g	2.45	6.84	8.19 (q, 2H, H2′, H6′) 7.32 (t, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 8.79$ $J_{F4'H2'} = J_{F4'H6'} = 5.39$ $J_{F4'H3'} = J_{F4'H5'} = 8.30$	
8h	2.47	6.88	8.12 (d, 2H, H2′, H6′) 7.62 (d, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 8.78$	
8i	2.43	6.84	7.99 (d, 2H, H2′, H6′) 7.75 (d, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 8.61$	
8j	2.43	6.83	7.97 (d, 2H, H2′, H6′) 7.82 (d, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 8.58$	
8k	2.50	6.95	8.09 − 8.22 (m, 4H, H2′, H3′, H5′, H6′)		
8l	2.36	6.75	7.60 (s, 1H, H2′) 7.09 (d, 1H, H5′) 7.80 (d, 1H, H6′)	$J_{5'6'} = 8.56$ $J_{2'6'} = 2.02$	3.93 (s, 3H, OCH_3) 3.90 (s, 3H, OCH_3)
8m	2.41	6.46	8.45 (d, 1H, H2′) 8.04 (d, 1H, H4′)	$J_{2'3'} = 8.51$ $J_{3'4'} = 8.24$	7.88 (d, 2H, Ar) $J = 7.42$; 7.46–7.64 (m, 3H, Ar)
8n	2.46	6.99	8.75 (s, 1H, H2′)		7.61–7.73 (dt, 2H, Ar) 7.95–8.08 (m, 4H, Ar)
8o	2.51	7.40	8.21 (d, 2H, H2′, H6′) 8.37 (d, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 9.12$	3.67 (s, 9H, $N^+(CH_3)_3$)
13	2.50 (s, 6H)	6.98 (s, 2H)	8.27 (s, 4H, H2′, H3′, H5′, H6′)		
16	2.53 (s, 9H)	7.14 (s, 3H)	9.01 (s, 3H, H2′, H4′, H6′)		

Nr.	*3-CH_3*	*2-CH*	*4-Ar Assignments*	*Coupling Constants /Hz*	*Additional Signals Assignments*
9e	2.16	6.11	7.76 (d, 2H, H2′, H6′) 7.27 (d, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 8.47$	1.35 (t, 3H, CH_2-CH_3) 2.99 (q, 2H, -CH_2-S) 16.19 (s, 1H, OHO)
9o	2.20	6.42	7.97 (d, 2H, H2′, H6′) 8.14 (d, 2H, H3′, H5′)	$J_{2'3'} = J_{5'6'} = 9.08$	3.73 (s, 9H, $N^+(CH_3)_3$) 15.96(s, 1H, OHO)
14	2.21 (s, 6H)	6.19 (s, 2H)	7.94 (s, 4H, H2′, H3′, H5′, H6′)		16.01 (s, 2H, OHO)
17	2.23 (s, 9H)	6.27 (s, 3H)	8.45 (s, 3H, H2′, H4′, H6′)		16.04 (s, 3H, OHO)

TABLE 4 Mass Spectroscopic Data of Some 4-Aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines (**8**). (In all spectra, an additional peak appears at *M*-133 except in the spectra of compound of **8k**; compounds **8o** and **16** exhibit no mol peaks.)

Nr.	*X*	M^+	M-15	M-19	M-105	M-X
8a	4-H	59, 100[a]	13[a]	14	52	100
8b	4-CH_3	92	100	12	63	100
8c	4-OCH_3	100	36	13	97	37
8d	4-SCH_3	100	45	15	76	40
8e	4-SC_2H_5	100	19	8	23	15
8f	4-$N(CH_3)_3$	100	34	26	55	35
8g	4-F	88	52	30	100	30
8h	4-Cl	28, 49[a]	32[a]	21[a]	100	45
8i	4-Br	100	37	11	65	74
8j	4-I	100	17	8	42	21
8k	4-NO_2	100	38	27	82	52[b]
8l	3,4-$(OCH_3)_2$	100	38	9	17	46
8m	2,3-Benzo	100	30	13	20	—
8n	3,4-Benzo	100	22	12	77	—
13		56	20	100[a]	92	52

[a]The peak appears at $m/z = M - 1$.
[b]The peak appears at $m/z = M + 1$.

borines **8** are, however, unstable. They hydrolyze therein into their corresponding aroylacetones **9**.

For transforming the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** into the corresponding aroylacetones **9** on a preparative scale, a procedure consisting of dissolving the starting 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** in methanol, adding a suitable base, such as triethylamine, refluxing the resulting mixture until no starting dioxaborines **8** are detectable, and cooling the mixture finally proves to be viable.

All of the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** and aroylacetones **9** prepared by the procedures described herein are depicted in Table 2.

The boron trifluoride-mediated condensation of acetophenones **6** with acetic anhydride **4a** can also be performed with multiple acetyl-substituted benzenes. Thus, 1,4-diacetyl-benzene **12** and 1,3,5-triacetyl-benzene **15**, e.g., can be transformed by the procedure described herein into their corresponding 2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborine derivatives **13** and **16**, respectively, which are hydrolyzable into the corresponding arylene bis- or tris-diketones **14** and **17**, respectively, by their reactions with methanol (Scheme 3).

The 2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborine derivatives **8**, **13**, and **16** and their corresponding 1,3-diketone derivatives **9**, **14**, and **17** have been characterized, insofar as they have not previously been described in the literature, by their elemental analyses as well as by their NMR and mass spectroscopic data. These data are compiled in the Tables 3–5 or posted in the Experimental section.

As seen from Table 3, the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** exhibit in their ^{1}H NMR spectra characteristic signals at $\delta \approx 2.25$–2.54, 6.70–7.40, and 6.79–9.02, which can be attributed to the protons in their methyl, dioxaborine, and aryl moieties, respectively. The same compounds **8** exhibit in their mass spectra, as shown in Table 4, mol peaks with high intensities. The assignment of most of the fragment peaks is simplified by their characteristic ^{10}B, ^{11}B isotopic pattern.

A characteristic feature of nearly all of the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8**, in contrast to the corresponding aroylacetones **9**, is their strong fluorescence. The corresponding data are summarized, together with the absorption data of some 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8**, in Table 6. The wavelengths and intensities of the fluorescence maxima parallel those of analogously substituted diaryl-substituted pyrylium salts **11** and can be detected, for most of the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8**, even in their solid states [6].

Moreover, the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8**, **13**, and **16** are, due to a high CH acidity at their dioxaborine-linked methyl groups that permit condensation of these compounds with, e.g., aromatic aldehydes or reactive formyl derivatives, good candidates for preparing deeply colored dyes [7]. Thus, they can be transformed into intensively colored styryl derivatives. Some of these compounds exhibit a strong fluorescence or a pronounced solvatochromism that allows use of these compounds as laser dyes [8] or as NLO-active compounds [9]. Due to their high electron affinity, the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines are able to form, with aromatic hydrocarbons, stable charge transfer complexes that can be used as photosentisizers for dimerizing 1,3-cyclodienes [10]. Moreover, the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines can be used, instead of their corresponding aroylacetones **9**, as synthons for preparing different types of heterocyclic compounds [11,12].

EXPERIMENTAL

Melting points were determined by using a Boetius heating-table microscope and are uncorrected. The ^{1}H NMR and mass spectra were recorded with a 300 MHz Varian Gemini 300 spectrometer and with an AMD 402 spectrometer, resp. using the EI technique

TABLE 5 Elemental Analytical Data of 2,2-Difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** and of the Aroylacetones **9e**, **9o**, **14**, and **17**

Nr.	*Formula (mol. mass)*	*Elemental Analyses*	*C*	*H*	*X*		*X*	
8a	$C_{10}H_9BF_2O_2$	calcd.	57.20	4.32				
	(209.99)	found	57.03	4.02				
8b	$C_{11}H_{11}BF_2O_2$	calcd.	58.98	4.95				
	(224.01)	found	58.98	4.40				
8c	$C_{11}H_{11}BF_2O_3$	calcd.	55.05	4.62				
	(240.01)	found	55.29	4.28				
8d	$C_{11}H_{11}BF_2O_2S$	calcd.	51.59	4.33	S	12.52		
	(256.07)	found	51.56	4.10		12.51		
8e	$C_{12}H_{13}BF_2O_2S$	calcd.	53.36	4.85	S	11.87		
	(270.10)	found	53.57	4.63		12.00		
8f	$C_{12}H_{14}BF_2NO_2$	calcd.	56.96	5.58	N	5.54		
	(253.06)	found	56.96	5.31		5.50		
8g	$C_{10}H_8BF_3O_2$	calcd.	52.69	3.54				
	(227.98)	found	52.55	3.10				
8h	$C_{10}H_8BClF_2O_2$	calcd.	49.14	3.30	Cl	14.50		
	(244.43)	found	49.28	3.49		14.56		
8i	$C_{10}H_8BBrF_2O_2$	calcd.	41.58	2.79	Br	27.66		
	(288.88)	found	41.52	2.34		27.59		
8j	$C_{10}H_9BF_2IO_2$	calcd.	35.65	2.38				
	(336.89)	found	36.13	2.27				
8k	$C_{10}H_8BF_2NO_4$	calcd.	47.10	3.16	N	5.49		
	(254.98)	found	47.44	3.10		5.48		
8l	$C_{12}H_{13}BF_2O_4$	calcd.	53.37	4.85				
	(270.04)	found	53.35	4.47				
8m	$C_{14}H_{11}BF_2O_2$	calcd.	64.66	4.26				
	(260.05)	found	64.62	3.96				
8n	$C_{14}H_{11}BF_2O_2$	calcd.	64.66	4.26				
	(260.05)	found	64.31	4.00				
8o	$C_{13}H_{17}ClBF_2NO_6$	calcd.	42.48	4.66	Cl	9.65	N	3.81
	(367.54)	found	42.64	4.83		9.61		3.90
13	$C_{14}H_{12}B_2F_4O_4$	calcd.	49.19	3.54				
	(341.86)	found	49.34	3.70				
16	$C_{18}H_{15}B_3F_6O_6$	calcd.	45.64	3.19				
	(473.73)	found	45.77	3.11				
9e	$C_{12}H_{14}O_2S$	calcd.	64.84	6.31	S	14.42		
	(222.30)	found	64.86	5.91		14.40		
9o	$C_{13}H_{18}ClNO_6$	calcd.	48.83	5.67	N	4.38		
	(319.74)	found	48.95	5.90		4.33		
14	$C_{14}H_{14}O_4$	calcd.	68.28	5.73				
	(246.26)	found	68.20	5.72				
17	$C_{18}H_{18}O_6$	calcd.	65.45	5.49				
	(246.26)	found	65.68	5.55				

TABLE 6 Absorption and Emission Data of Some 2,2-Difluoro-6-methyl-1,3,2-(2H)-dioxaborines

Nr. *X*	**8a** *H*	**8c** CH_3O	**8d** SCH_3	**8f** $N(CH_3)_2$	**8h** *Cl*
$\lambda_{max,\ Abs}$[a]	328	359	381	422	335
lg ε	4.47	4.66	4.63	4.46	4.78
$\lambda_{max,\ Fl}$	—	390[b] [24]	431[a], 443[b]	472[b]	≈410[a]

[a]In chloroform.
[b]In dichloromethane.

at 70 eV. The PM3 calculations were performed with the program MOPAC 6.0 using standard parameters.

Determination of the Extent of Reaction in the Condensation of Substituted Acetophenones **6** *with Acetic Anhydride* **4a** *in the Presence of the Boron Trifluoride—Acetic Acid—Complex* **7**

A mixture of 10 mmol of a substituted acetophenone **6**, 20 mmol (2.04 g) of acetic anhydride **4a**, and 6.8 mmol (1.28 g) of boron trifluoride—acetic acid—complex **7** was heated on a steam bath. After 20 min-

utes, 0.1 mL of the resulting mixture was separated and added to a mixture of 0.7 mL of deuterochloroform, 0.15 mL of acetic anhydride **4a** and 0.15 mL of boron trifluoride—acetic acid—complex **7** (**4a** and **7** were added to promote a better solubility of the reaction products). Subsequently, the intensities of the methyl signals of the reaction components in the mixture were estimated by means of ^{1}H NMR spectroscopy. The methyl signals of the newly formed 2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** and 4,6-diaryl-2-methyl-pyrylium-tetrafluoroborates **11** as well as the methyl signals of the starting acetophonones **7**, were monitored at about $\delta \approx 2.30$, 2.80–3.20, and 2.60, respectively. In the case of the acetophenones **6d** and **6e**, the methyl signals were monitored at $\delta = 2.80$. The methyl signals of the starting acetic anhydride **4a** and boron trifluoride—acetic acid—complex **7** coincided at $\delta = 2.17$ and could, therefore, not be analyzed.

The results of the ^{1}H NMR-spectroscopic measurements have been summarized in Table 1.

Optimized Synthesis of 4-Aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8**

To a mixture of 0.2 mol (37.6 g) of boron trifluoride—acetic acid—complex **7** and 0.6 mol (61.2 g) of acetic anhydride **4a**, 0.1 mol of the appropriate acetophenone **6** was added dropwise under stirring at 45 °C during a period of 6 to 8 hours. (For the preparation of the dioxaborine **8f** 0.3 mol (56.3 g) of boron trifluoride—acetic acid—complex **7** must be used because the dimethylamino group in the educt consumes one equivalent of boron trifluoride before it starts the acylation reaction). Solid acetophenones **6** were dissolved or suspended in some acetic anhydride before their addition. After the acetophenone addition, the reaction mixture was stirred for 3 more hours and then allowed to stand until the precipitation of product was completed. The product formed was isolated by suction filtration, washed with acetic acid, ethyl acetate, and diethyl ether. After drying, it was recrystallized.

In the case of the preparation of the compounds **8f** or **8o**, the resulting reaction mixture was concentrated under vacuum and subsequently diluted with some methanol under cooling. The precipitate formed was separated by suction filtration, washed with methanol, and recrystallized from acetic acid.

The yields and melting points of the 4-aryl-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **8** so obtained are depicted in Table 2.

By the same method of preparation as described and by starting with 0.05 mol (8.1 g) of 1,4-diacetylbenzene **12**, and 0.033 mol (6.8 g) of 1,3,5-triacetylbenzene **15**, the tris- and bis-2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborines **13** and **16** were obtained.

Preparation of Substituted Aroylacetones **9**, **14**, *and* **17** (*General Procedure*)

A suspension of 25 mmol of an appropriate 2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborine **8**, **13**, or **16**, in 70 mL of methanol and 3 mL of triethylamine was refluxed until all of the starting material had dissolved. Then water was added to the mixture until the 1,3-diketones **9**, **14**, and **17** formed started to crystallize. After concentration and cooling, the product that had precipitated was isolated by suction filtration, washed with water, and dried.

The yields and melting points of the aroylacetones **9** so obtained are depicted in Table 2.

CAS Reg. Nr. (RN) of compounds **9** that are already known but for which no melting points are reported are **9d** RN: 128172-84-9 and **9j** RN: 54454-25-0.

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