formation of the ester from the *neutral* reactants (1.2×10^4). The corresponding equilibrium constant for formation of 4-nitrophenyl acetate from acetylimidazole and 4-nitrophenol is 1.1.[6] Imidazole is thus a very efficient reagent for phosphorylation reactions to phenols and presumably to alcohols. The scope of the reagent is restricted by the pK_a of the phenol. The value of β_{eq} for the reaction of cation with anion is 1.87 so that it may be calculated that the equilibrium constant for formation will be unity for a phenol with $pK_{ArOH} = 4.34$. The reagent is therefore not effective for strongly acidic phenols. The fact that we found no reaction between 2,4-dinitrophenol and the *N*-(diethoxyphosphoryl)imidazole is presumably due to the equilibrium constant being too low for sufficient reaction to occur under the conditions prevailing.

Acknowledgment. We are grateful to the Government of Saudi Arabia (S.A.B.) and to S.E.R.C. (U.K.) (Grant GR/E/06558) for financial support.

Supplementary Material Available: Analytical and physical data for the aryl diethyl phosphate esters (1 page). Ordering information is given on any current masthead page.

Isolation and Reaction of New Aromatic Dications. 4-Thioniapyridinium Dications: 2-Aryl-(or 2-Alkyl-)4-methyl-3-oxo-2*H*-1,4-thiazin-2-ylium Tetrafluoroborates

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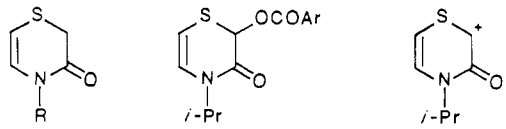
2-Hydroxy-4-methyl-2-aryl(or -2-*tert*-butyl)-2*H*-1,4-thiazin-3-ones (**5**) generate carbocations **6** in trifluoroacetic acid solution at room temperature. These ions are sufficiently stable to be observed spectroscopically in this solution. Reaction of **6** with some nucleophiles are described. Stable crystalline tetrafluoroborates of **6** were isolated. From ^1H NMR, ^{13}C NMR, and UV–vis spectral data it was concluded that these cations are aromatic in nature and should be depicted as **9** and called 4-thioniapyridinium dications.

In the course of our investigation on the chemistry of 4-alkyl-2*H*-1,4-thiazin-3-ones **1**[1] and their derivatives,[2] in search for some biological activities of these compounds, it was found that reactions of esters **2**[3] with various nucleophiles occurred with exclusive alkyl–oxygen bond fission.[4] It was also found that the ester **2** (Ar = *m*-ClC_6H_4) is readily solvolyzed in various kinds of solvents and give *m* values as high as 1.53[5] for this compound in Grunwald–Winstein equation,[6] $\log k - \log k_0 = mY$. Since by definition $m = 1.00$ for *tert*-butyl chloride, the value 1.53 means solvolysis of the ester **2** (Ar = *m*-ClC_6H_4) is much more sensitive to the change in polarity of the solvents than is *tert*-butyl chloride.



1 **2**, Ar = Ph, *m*-ClC_6H_4 **3**

These facts strongly imply intermediacy of a very stable carbocationic species **3** during these nucleophilic displacements of the ester **2**. The generation and therefore its unusual stability of the ion **3** seemed quite surprising, since **3** is a secondary carbenium ion and its cationic center is directly linked to a carbonyl carbon. With this situation in mind the present work was undertaken to clarify structure and nature of the ion **3**, by observing it directly in strongly acidic media and if possible by isolating it as a stable salt.

Table I. Reaction of Grignard Reagents (R′MgX) with Diketone 4[4]

product	R	R′	yield, %	mp, °C	IR, cm^{-1}
5a	H	Ph	60	152	1628
5b	H	*p*-FC_6H_4	65	118	1634
5c	H	*p*-ClC_6H_4	58	137	1637
5d	H	*p*-MeC_6H_4	65	153	1628
5e	H	*p*-$MeOC_6H_4$	50	138	1645
5f	Me	Ph	100	145	1640
5g	Me	*p*-$MeOC_6H_4$	55	141	1620
5h	H	Me	56	oil	1640
5i	H	Et	74	oil	1628
5j	H	*t*-Bu	34	81	1617

Results and Discussion

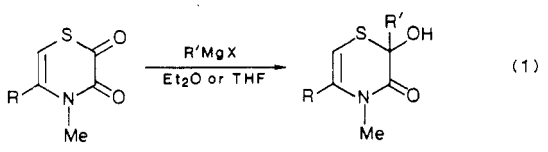
Preparation of 2-Substituted 2-Hydroxy-4-methyl-2*H*-1,4-thiazin-3-ones (5). Attempted direct observation of the carbocation **3** failed; it proved insufficiently stable to exist in trifluoroacetic acid (TFA) at room temperature. Therefore 2-aryl-(and some 2-alkyl-)substituted cations **6** were chosen for present study.

Reaction of diketones **4**[4] with various alkyl- and arylmagnesium halides proceeded with perfect regioselectivity in ether or tetrahydrofuran as solvent at room temperature to give corresponding 3-keto 2-alcohols **5** as sole products. The results are shown in Table I.

Generation of Cations 6a–g in TFA from Corresponding Alcohols 5a–g. 2-Aryl-substituted keto alcohols

(1) Hojo, M.; Masuda, R.; Kohsaka, S.; Nagase, K. *Synthesis* **1979**, 272.
(2) Masuda, R.; Hojo, M.; Ichi, T.; Adachi, F.; Yoshinaga, K. *Phosphorus Sulfur* **1983**, *16*, 143.
(3) Hojo, M.; Masuda, R.; Yoshinaga, K.; Munehira, S. *Synthesis* **1982**, 312.
(4) Hojo, M.; Masuda, R.; Ichi, T.; Yoshinaga, K.; Munehira, S.; Yamada, M. *Synthesis* **1982**, 424.
(5) Hojo, M.; Masuda, R.; Ichi, T.; Yoshinaga, K.; Yamada, M. *Tetrahedron Lett.* **1982**, 4963.
(6) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.

0022-3263/88/1953-2209$01.50/0

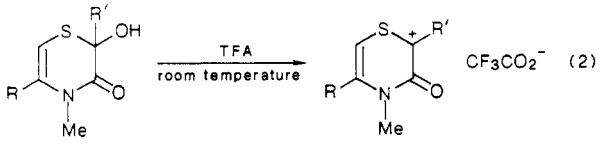


(1)

4a, R = H
4b, R = Me

5a–j

5 were dissolved in TFA at room temperature, which imparted yellow (**5a,b**), red (**5c,d**), and purple (**5e**) colors. The electronic absorption spectra of these solutions, quite different from those taken in methanol, showed intense bands in visible region (Table II), implying generation of stable carbocationic species **6**.



(2)

5 **6**

a, R = H, R′ = Ph; **b**, R = H, R′ = *p*-FC_6H_4; **c**, R = H, R′ = *p*-ClC_6H_4; **d**, R = H, R′ = *p*-MeC_6H_4; **e**, R = H, R′ = *p*-$MeOC_6H_4$; **f**, R = Me, R′ = Ph; **g**, R = Me, R′ = *p*-$MeOC_6H_4$; **j**, R = H, R′ = *t*-Bu

^{1}H and ^{13}C NMR Spectra of the Cation 6. Data of ^{1}H NMR chemical shifts for the cations **6** recorded in TFA as solvent are listed in Table III. As is seen in Table III, signals for the protons at the 5-position of cations **6** appeared in the range of δ 8.30 (R′ = *p*-$MeOC_6H_4$) to 8.69 (R′ = Ph) and showed large downfield shifts of 2.12 (R′ = *p*-$MeOC_6H_4$) to 2.59 (R′ = Ph) ppm compared to those of corresponding precursor keto alcohols **5**. Large downfield shifts (1.9–2.4 ppm) can also be seen with the protons at the 6-position. These δ values, together with the data of electronic spectra mentioned above, strongly suggest that the positive charge of **6** is widely delocalized over this heterocyclic system, and this system is an aromatic cation in nature. Possible structures (canonical forms) for this heterocyclic system **6** can be represented as shown in Scheme I in which B–E are contributing the most, and this new aromatic dication **7** may be called as 1,4-thiazinium dication or 4-thioniapyridinium (2-oxido-4-thioniapyridinium) dication. In contrast, the corresponding downfield shifts for protons of the benzene rings of **6** are relatively small. They are 0.6–1.0 ppm for the 2′-positions and about 0.4 ppm for the 3′-positions.

In Table IV are shown ^{13}C NMR chemical shifts for the cation **6** measured in TFA at −10 °C. These data also indicate strong delocalization of the positive charge (16–21 ppm for C-5 and 7–11 ppm for C-6. See Table IV and supplementary material). Regarding this delocalization, comparison of the present cation **6a** with trityl cation seems of particular interest. The ^{13}C chemical shift of the carbon at the 2-position of **6a** is δ 173.5, which is about 40 ppm in upfield compared to that for the central carbon of trityl cation in TFA (δ 211.6).[7] On the other hand, the δ values for C-1′ (133.5), C-2′ (131.8), and C-4′ (139.2) are smaller than those for C-1 (140.1), C-2 (142.4), and C-4 (143.5) of trityl cation in TFA.[7]

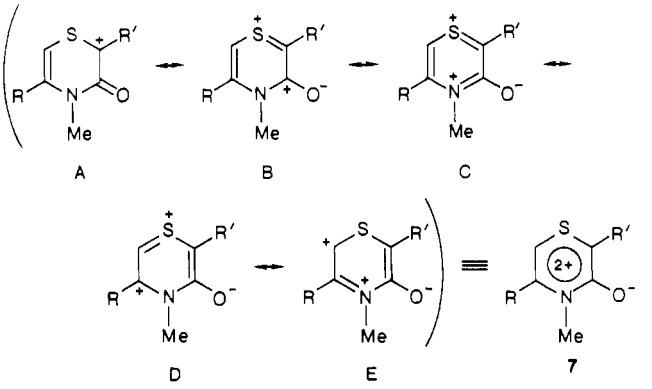
2-Alkyl-Substituted Cations 6h–j. On dissolution of 2-methyl and 2-ethyl keto alcohols **5h** and **5i** into TFA at room temperature there occurred extensive deterioration, presumably by deprotonation from the expected carbocationic species and subsequent reactions of the resulting olefins. As anticipated 2-*tert*-butyl keto alcohol **5j** gave corresponding cation **6j** in TFA at room temperature. The relevant spectroscopic data are in Tables II–IV.

(7) Hojo, M.; Ichi, T., unpublished data.

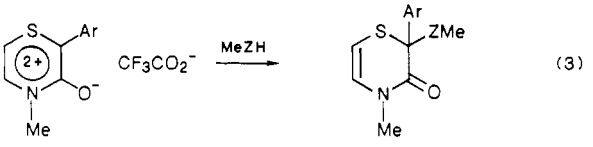
Table II. UV and Visible Absorption Spectra of the Cation 6 in TFA at Room Temperature.

cation	R	R′	λ_{max}, nm (ε)	
6a	H	Ph	479 (13900)	347 (1300)
6b	H	*p*-FC_6H_4	487 (15900)	351 (1600)
6c	H	*p*-ClC_6H_4	496 (18600)	361 (1300)
6d	H	*p*-MeC_6H_4	505 (22500)	356 (1700)
6e	H	*p*-$MeOC_6H_4$	554 (28000)	372 (1100)
6f	Me	Ph	477 (9600)	336 (1500)
6j	H	*t*-Bu	408 (7500)	

Scheme I. Possible Structure for the Cation 6 (R = H or Me; R′ = *t*-Bu or Ar)



Reaction of Cations 6 with Nucleophiles. A solution of cation **6a** in TFA was poured into methanol at room temperature. The reaction proceeded quite regioselectively and gave 2-methoxy-substituted compound **8a** as a sole product. None of the 5- or 6-substituted derivatives were detected. The results are listed in Table V.

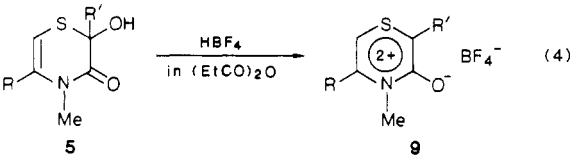


(3)

6a, Ar = Ph
6e, Ar = *p*-$MeOC_6H_4$

8a, Ar = Ph, Z = O
8e, Ar = *p*-$MeOC_6H_4$, Z = O
8k, Ar = *p* $MeOC_6H_4$, Z = S

Isolation of Tetrafluoroborates 9 of Cations 6. Treatment of alcohols **6** with tetrafluoroboric acid in propionic anhydride as solvent gave corresponding tetrafluoroborates **9** of cations **6** as beautiful crystals red to purple in color. These salts are stable enough in the dry

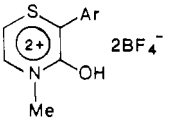


(4)

5 **9**

d, R = H, R′ = *p*-MeC_6H_4; **e**, R = H, R′ = *p*-$MeOC_6H_4$; **f**, R = Me, R′ = Ph; **j**, R = H, R′ = *t*-Bu

air and can be stored for more than one month at room temperature without any deterioration. The yields and melting points are listed in Table VI. Data for elemental analysis of the salt **9e** agreed well with the suggested structure **9** and not with 3-hydroxy structure **10**. ^{1}H NMR



10, Ar = *p*-$MeOC_6H_4$

spectra of the isolated salts **9** were taken in CD_3NO_2 as

Table III. ^{1}H NMR Chemical Shifts (δ) of Cations 6 ($Y^- = CF_3CO_2^-$) in TFA and Tetrafluoroborates 9 ($Y^- = BF_4^-$) in CD_3NO_2 (35 °C)

				δ						
ion	R	R′	Y^-	5-H	6-H	2′-H	3′-H	4′-Me(O)	NMe	5-Me
6a	H	Ph	$CF_3CO_2^-$	8.69		8.26–7.40[a]			4.03	
6b	H	*p*-FC_6H_4	$CF_3CO_2^-$	8.65	7.86	8.45–8.24[b]	7.60–7.20[b]		4.02	
6c	H	*p*-ClC_6H_4	$CF_3CO_2^-$	8.62	7.87	8.09	7.62		4.02	
6d	H	*p*-MeC_6H_4	$CF_3CO_2^-$	8.57	7.78	8.15	7.52	2.57[c]	4.03	
6e	H	*p*-$MeOC_6H_4$	$CF_3CO_2^-$	8.30	7.51	8.49	7.23	4.13[d]	3.98	
6f	Me	Ph	$CF_3CO_2^-$		7.78	8.18–7.35[e]			3.97	2.90
6g	Me	*p*-$MeOC_6H_4$	$CF_3CO_2^-$		7.42	8.34	7.19	4.06[d]	3.92	2.81
6j	H	*t*-Bu[f]	$CF_3CO_2^-$	8.70	7.80				3.92	
9d	H	*p*-MeC_6H_4	BF_4^-	8.60	7.78	8.06	7.43	2.48[c]	3.87	
9e	H	*p*-$MeOC_6H_4$	BF_4^-	8.52–8.16[g]	7.58	8.52–8.16[g]	7.17	4.03[d]	3.87	
9f	Me	Ph	BF_4^-		7.76	8.18–7.29[e]			3.86	2.85
9j	H	*t*-Bu[h]	BF_4^-	8.64	7.76				3.81	

[a] 6-H and phenyl protons. [b] Multiplets due to H–F coupling. [c] Para Me. [d] Para MeO. [e] Phenyl protons. [f] δ 1.70 for *t*-Bu. [g] 5-H and 2′-H protons. [h] δ 1.62 for *t*-Bu.

Table IV. ^{13}C NMR Data of Cations 6 in TFA at −10 °C[a]

			chemical shifts, ppm								
ion	R	R′	2-C	3-C	5-C	6-C	1′-C	2′-C	3′-C	4′-C	NMe
6a	H	Ph	173.5	156.3	149.4	112.3	133.5	131.8	131.3	139.2	43.8
					(190.4)	(202.6)		(167.2)	(166.0)	(163.6)	(146.5)
6b	H	*p*-FC_6H_4	171.9	156.1	149.2	111.7	129.9	135.2[b]	119.2[c]	170.6[d]	43.9
					(192.9)	(196.5)		(164.8)	(168.5)		(147.7)
6c	H	*p*-ClC_6H_4	171.0	155.5	149.3	111.4	131.4	132.7	131.5	149.3	43.6
					(189.2)	(201.4)		(168.5)	(170.9)		(145.3)
6d[e]	H	*p*-MeC_6H_4	173.4	155.9	147.8	110.3	131.7	132.4	132.4	154.2	43.3
					(186.8)	(199.0)		(166.0)	(166.0)		(144.0)
6e[f]	H	*p*-$MeOC_6H_4$	171.2	156.7	144.9	109.2	128.9	136.7	118.4	172.8	43.6
					(192.9)	(197.8)		(166.0)	(169.7)		(143.4)
6g[g,h]	Me	*p*-$MeOC_6H_4$	167.1	157.9	157.3	108.9	128.3	135.6	118.1	171.3	37.0
						(194.1)		(167.8)	(164.8)		(145.8)
6j[i]	H	*t*-Bu	194.0	155.3	151.2	110.9					43.3
					(190.4)	(200.2)					(145.2)

[a] Chemical shifts are given in ppm from internal TMS. In parentheses are C–H coupling constants (in Hz). [b] J_{CF} = 11.0 Hz. [c] J_{CF} = 22.0 Hz. [d] J_{CF} = 267.3 Hz. [e] 22.6 ppm (J = 128.2 Hz) for para Me. [f] 57.7 ppm (J = 146.5 Hz) for *p*-MeO. [g] 57.5 ppm (J = 144.1 Hz) for para MeO. [h] 24.7 ppm (J = 130.6 Hz) for 5-Me. [i] 48.1 and 28.6 ppm (J = 129.4 Hz) for *t*-Bu.

Table V. Reaction of the Cation 6 with Some Nucleophiles

ion	R	R′	MeZH	conditions[a]	product	yield, %
6a	H	Ph	MeOH	rt/1 h	**8a**	75
6e	H	*p*-$MeOC_6H_4$	MeOH	rt/1 h	**8e**	93
6e	H	*p*-$MeOC_6H_4$	MeSH	0 °C/0.5 h	**8k**	90

[a] rt = room temperature.

Table VI. Isolation of the Cation as Tetrafluoroborates 9

cation	R	R′	yield, %	mp, °C
9d	H	*p*-MeC_6H_4	52	72
9e	H	*p*-$MeOC_6H_4$	85	68–70
9f	Me	Ph	54	70–71
9j	H	*t*-Bu	68	*a*

[a] Hygroscopic.

solvent (Table III), all of which are essentially the same as those of the corresponding cations **6** generated in TFA as solvent.

Experimental Section

Melting points were determined in capillary tubes in a silicon oil (Shin-Etsu Chemicals, KF-54) bath and were not corrected. Microanalyses were performed in the Kyoto University Micro-Analysis Laboratory. ^{1}H NMR spectra were recorded either on a Hitachi R-24 (60 MHz) or a JEOL PMX-60SI (60 MHz) spectrometer. ^{13}C NMR spectra were recorded on a JEOL PFT-100 spectrometer. IR spectra were recorded on a Hitachi EPI-G3 spectrophotometer. UV and visible absorption spectra were recorded on a Hitachi 200-18 spectrophotometer. Commercial diethyl ether and THF were dried and distilled over sodium and finally distilled from $LiAlH_4$ prior to use.

2,4-Dimethyl-1,3-thiazole.[8,9] A mixture of thioacetamide (26.2 g, 0.348 mol) and monochloroacetone (32.2 g, 0.348 mol) in benzene was refluxed for 1 h. The reaction mixture was extracted with water, and the water layer was made alkaline and extracted with CH_2Cl_2. The organic layer was dried and evaporated to yield 36.9 g (97%) of the product as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3 H, 4-Me), 2.65 (s, 3 H, 2-Me), 6.64 (s, 1 H, 5-H).

2,3,4-Trimethyl-1,3-thiazolium Iodide. A mixture of 2,4-dimethyl-1,3-thiazole (21.5 g, 0.19 mol) and methyl iodide (81.2 g, 0.57 mol) in acetone (100 mL) was refluxed for 1 day. Precipitated crystals were collected on a glass filter, washed with acetone, and dried in vacuo to leave 46.0 g (95%) of the product as white crystals: mp (MeOH) 265 °C; IR (KBr) 1587, 1486, 1353, 1168, 1035, 800, 778 cm^{-1}; ^{1}H NMR (CF_3CO_2H) δ 2.61 (s, 3 H, 4-Me), 2.98 (s, 3 H, 2-Me), 4.04 (s, 3 H, NMe), 7.45 (s, 1 H, 5-H). Anal. Calcd for $C_6H_{10}NSI$: C, 12.25; H, 3.95; N, 5.49; I, 49.74. Found: C, 28.47; H, 4.10; N, 5.41; I, 49.53.

2-(Iodomethyl)-3,4-dimethyl-1,3-thiazolium Iodide. To a suspension of 2,3,4-trimethyl-1,3-thiazolium iodide (9.74 g, 38.2 mmol) in CH_2Cl_2 (100 mL) were added iodine (9.69 g, 38.2 mmol) and then dropwise a dichloromethane solution (50 mL) of triethylamine (5.80 g, 57.3 mmol), and the reaction mixture was stirred for 0.5 h at room temperature. Precipitates were collected on a glass filter, washed with acetone, and dried to yield 14.2 g (98%) of the product as yellow crystals. This material is practically pure for subsequent preparations and is not stable enough to be stored for long period, so it is recommended to prepare just before use. Recrystallization from water gave pure material: mp 242–243 °C; IR (KBr) 1580, 1472, 1265, 1030, 1022, 885, 760 cm^{-1}; ^{1}H NMR (TFA) δ 2.65 (s, 3 H, 4-Me), 3.96 (s, 3 H, NMe), 4.95

(8) Hantzsch, A. *Justus Liebigs Ann. Chem.* **1889**, *250*, 265.
(9) Clarke, H. T.; Gurin, S. *J. Am. Chem. Soc.* **1935**, *57*, 1876.

(s, 2 H, CH_2), 7.64 (s, 1 H, 5-H). Anal. Calcd for $C_6H_9NSI_2$: C, 18.91; H, 2.38; N, 3.68; I, 66.61. Found: C, 18.93; H, 2.50; N, 3.60; I, 66.52.

4,5-Dimethyl-(2*H*)-1,4-thiazin-3(4*H*)-one. To an ice-cooled suspension of 2-(iodomethyl)-3,4-dimethyl-1,3-thiazolium iodide, (13.8 g, 36.2 mmol) was added a solution of KOH (6 g in 5 mL water). The mixture was stirred for 1 h at room temperature and extracted with CCl_4 (Dichloromethane is not recommended for this extraction). The combined extracts were dried (Na_2SO_4) and evaporated in vacuo to leave 5.08 g (98%) of the crude product as a brown oil, which was distilled in vacuo to give pure material (3.14 g, 61%): bp 160 °C (oven temperature) (10 mmHg) [lit.[10] bp 98 °C (0.6 mmHg)]; IR 1662 (C=O), 1355, 1332, 1120, 935, 823, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.02 (s, 3 H, 5-Me), 3.15 (s, 3 H, NMe), 3.24 (s, 2 H, CH_2), 5.47 (s, 1 H, 6-H). Anal. Calcd for C_6H_9ONS: C, 50.32; H, 6.33; N, 9.78; S, 22.39. Found: C, 50.51; H, 6.45; N, 9.71; S, 22.37.

2,2-Dimethoxy-4,5-dimethyl-(2*H*)-1,4-thiazin-3(4*H*)-one. A mixture of 4,5-dimethyl-2*H*-1,4-thiazin-3-one (856 mg, 5.98 mmol) and benzoyl peroxide (2.89 g, 12 mmol) in methanol (30 mL) was refluxed for 5 h. Evaporation of the solvent from the reaction mixture in vacuo was followed by dissolution of the residue in CH_2Cl_2 and the solution was washed (aqueous Na_2CO_3 and water) and dried (Na_2SO_4). Evaporation of the solvent in vacuo left a yellow oil (1.51 g). Chromatography on silica gel using benzene–ethyl acetate (9:1) as the eluent gave a pale yellow oil (855 mg, 70%), which was essentially pure by ^1H NMR and used for preparation of diketone **4b** without further purification: bp 220 °C (oven temperature) (10 mmHg); IR 1665 (C=O), 1355, 1310, 1120, 1065, 870, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03 (s, 3 H, 5-Me), 3.16 (s, 3 H, NMe), 3.42 (s, 6 H, OMe), 5.31 (s, 1 H, 6-H).

4,5-Dimethyl-2*H*-1,4-thiazine-2,3(4*H*)-dione (4b). To a solution of 2,2-dimethoxy-4,5-dimethyl-2*H*-1,4-thiazin-3-one (855 mg, 4.2 mmol) in acetone (5 mL) was added a few drops of concentrated HCl and the mixture was stirred for 0.5 h at room temperature. The reaction mixture was dried (Na_2SO_4) and evaporated in vacuo to yield 667 mg (100%) of the product as yellow crystals: mp (CCl_4) 127 °C; IR (KBr) 1660, 1600, 1407, 1307, 1085, 890, 800, 635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.26 (s, 3 H, 5-Me), 3.47 (s, 3 H, NMe), 5.65 (s, 1 H, 6-H). Anal. Calcd for $C_6H_7NO_2S$: C, 45.85; H, 4.49; N, 8.91; S, 20.40. Found: C, 45.64; H, 4.20; N, 8.69; S, 20.20.

2-Hydroxy-4-methyl-2-phenyl-2*H*-1,4-thiazin-3(4*H*)-one (5a). To a Grignard reagent made from bromobenzene (635 mg, 4.04 mmol) and magnesium (98 mg, 4.03 mmol) in THF (tetrahydrofuran) was added dropwise diketone **4a** (193 mg, 1.35 mmol) in THF (5 mL), and the reaction mixture was stirred for 3 h at room temperature. After hydrolysis with dilute HCl the reaction mixture was extracted with CH_2Cl_2. The combined extracts were washed with water and dried (Na_2SO_4), and the solvent was removed to leave the raw product (353 mg) as a brown solid. Chromatography on silica gel using benzene–ethyl acetate (8:2) as the eluent yielded **5a** (178 mg, 60%) as light brown crystals. Recrystallization from benzene gave white crystals: mp 152 °C; UV (EtOH) 289 (ϵ 2700), 221 (6800) nm; IR (KBr) 3310 (OH), 1628 (C=O), 1390, 1265, 1092, 1040, 1003, 746, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.25 (s, 3 H, NMe), 4.74 (br s, 1 H, OH), 5.54 (d, 1 H, J = 7.2 Hz, 6-H), 6.09 (d, 1 H, J = 7.2 Hz, 5-H), 7.15–7.66 (m, 5 H, Ph). Anal. Calcd for $C_{10}H_{11}NO_2S$: C, 59.71; H, 5.01; N, 6.33; S, 14.49. Found: C, 59.57; H, 4.91; N, 6.27; S, 14.43.

2-(*p*-Fluorophenyl)-2-hydroxy-4-methyl-2*H*-1,4-thiazin-3(4*H*)-one (5b). The same procedure as above with the use of *p*-fluorobromobenzene (1.9 g, 10.9 mmol) and diketone **4a** (500 mg, 3.5 mmol) gave crystals (1.40 g). Chromatography (silica gel; benzene–ethyl acetate, 9:1) yielded the alcohol **5b** (542 mg, 65%): mp 117–118 °C (benzene); IR (KBr) 3240 (OH), 1634 (C=O), 1510, 1395, 1335, 1232, 1158, 1055, 868, 823, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.26 (s, 3 H, NMe), 4.76 (s, 1 H, OH), 5.58 (d, 1 H, 6-H), 6.16 (d, 1 H, 5-H), 6.8–7.2 (m, 2 H, Ar), 7.3–7.8 (m, 2 H, Ar). Anal. Calcd for $C_{11}H_{10}NOSF$: C, 55.22; H, 4.21; N, 5.85; F, 7.94. Found: C, 55.12; H, 3.97; N, 5.80; F, 7.98.

2-(*p*-Chlorophenyl)-2-hydroxy-4-methyl-2*H*-1,4-thiazin-3(4*H*)-one (5c). As described above, *p*-chlorobromobenzene (2.1 g, 11.0 mmol) and diketone **4a** (500 mg, 3.5 mmol) gave a brown solid (1.34 g), and chromatography of which (silica gel; benzene–ethyl acetate, 9:1) yielded the alcohol **5c** as white crystals (519 mg, 58%): mp 136–137 °C (benzene); UV (EtOH) 286 (ϵ 1100), 220 (6500) nm; IR (KBr) 3240 (OH), 1637 (C=O), 1495, 1400, 1330, 1090, 1052, 1008, 860, 815, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.24 (s, 3 H, NMe), 4.80 (s, 1 H, OH), 5.59 (d, 1 H, 6-H), 6.19 (d, 1 H, 5-H), 7.35 (AB q, 4 H, Ar). Anal. Calcd for $C_{11}H_{10}NOSCl$: C, 51.67; H, 3.94; N, 5.48; S, 12.54; Cl, 13.86. Found: C, 51.77; H, 3.88; N, 5.45; S, 12.38; Cl, 13.99.

2-Hydroxy-4-methyl-2-*p*-tolyl-2*H*-1,4-thiazin-3(4*H*)-one (5d). The same procedure as the 2-phenyl case, with the use of *p*-bromotoluene (430 mg, 2.51 mmol), magnesium (61 mg, 2.51 mmol), and diketone **4a** (120 mg, 0.838 mmol), afforded a brown oil (320 mg). Chromatography (silica gel; benzene–ethyl acetate, 8:2) yielded the product **5d** as pale yellow crystals (120 mg, 64.7%). Recrystallization (benzene) gave the pure alcohol as white crystals: mp 153 °C; UV (EtOH) 290 (ϵ 2700), 227 (8500) nm; IR (KBr) 3300 (OH), 1628 (C=O), 1515, 1390, 1265, 1180, 1050, 1005, 810, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.34 (s, 3 H, para Me), 3.28 (s, 3 H, NMe), 4.51 (br s, 1 H, OH), 5.57 (d, 1 H, J = 7.2 Hz), 6.13 (d, 1 H, J = 7.2 Hz, 5-H), 7.08 (d, 2 H, J = 7.8 Hz, Ar), 7.41 (d, 2 H, J = 7.8 Hz, Ar).

2-Hydroxy-2-(*p*-methoxyphenyl)-4-methyl-2*H*-1,4-thiazin-3(4*H*)-one (5e). Starting from *p*-bromoanisole (1.18 g, 6.29 mmol) and diketone **4a** (300 mg, 2.10 mmol), the same procedure as described above gave raw product (710 mg), and chromatography (silica gel; benzene–ethyl acetate, 7:3) afforded **5e** (260 mg, 49%) as light brown crystals. Recrystallization from benzene gave pure alcohol as white crystals: mp 138 °C; IR (KBr) 3260 (OH), 1645 (C=O), 1258, 1178, 1063, 823, 815, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.28 (s, 3 H, NMe), 3.80 (s, 3 H, OMe), 5.62 (d, 1 H, 7.2 Hz, 6-H), 6.18 (d, 1 H, J = 7.2 Hz, 5-H), 6.88 (d, 2 H, J = 8.4 Hz, 3′-H), 7.48 (d, 2 H, J = 8.4 Hz, 2′-H). Anal. Calcd for $C_{12}H_{13}NO_3S$: C, 57.45; H, 5.21; N, 5.62; S, 12.59. Found: C, 57.35; H, 5.21; N, 5.57; S, 12.76.

2-Hydroxy-4,5-dimethyl-2-phenyl-2*H*-1,4-thiazin-3(4*H*)-one (5f). As described above, bromobenzene (646 mg, 4.11 mmol) and diketone **4b** (250 mg, 1.59 mmol) gave 969 mg (100%) of **5f** as a brown solid. Recrystallization ($CHCl_3$) afforded pure alcohol as light brown crystals: mp 145 °C; UV (EtOH) 290 (ϵ 2300), 212 (9600) nm; IR (KBr) 3330 (OH), 1640 (C=O), 1445, 1390, 1330, 1130, 1040, 885, 770, 745, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.92 (s, 3 H, 5-Me), 3.32 (s, 3 H, NMe), 4.99 (s, 1 H, OH), 5.34 (s, 1 H, 6-H), 7.63–7.12 (m, 5 H, Ph). Anal. Calcd for $C_{12}H_{13}O_2NS$: C, 61.25; H, 5.57; N, 5.95; S, 13.63. Found: C, 61.25; H, 5.53; N, 5.72; S, 13.39.

2-Hydroxy-2-(*p*-methoxyphenyl)-4,5-dimethyl-2*H*-1,4-thiazin-3(4*H*)-one (5g). Starting from *p*-bromoanisole (715 mg, 3.82 mmol) and diketone **4b** (200 mg, 1.27 mmol), the same procedure as described above gave the raw product (308 mg). Chromatography (silica gel, CH_2Cl_2) afforded 184 mg (55%) of **5g** as light brown crystals. Recrystallization from hexane–chloroform gave pure crystals: mp 138–141 °C; IR (KBr) 3300 (OH), 1620 (C=O), 1510, 1305, 1255, 1180, 1123, 1040, 1020, 885, 833, 813, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.90 (s, 3 H, 5-Me), 3.30 (s, 3 H, NMe), 3.76 (s, 3 H, OMe), 5.33 (s, 1 H, 6-H), 7.07 (AB q, 4 H, Ar).

2-Hydroxy-2,4-dimethyl-2*H*-1,4-thiazin-3(4*H*)-one (5h). To an ethereal solution (10 mL) of methylmagnesium iodide made from methyl iodide (357 mg, 2.52 mmol) and magnesium (61 mg, 2.51 mmol) was added diketone **4a** (120 mg, 0.838 mmol) in THF (5 mL). After the mixture was stirred for 3 h at room temperature, usual workup left 75 mg (56%) of crude alcohol as a brown oil. Chromatography on silica gel (benzene–ethyl acetate, 7:3) yielded 50 mg (38%) of **5h** as an oil: IR (neat) 3330 (OH), 1640 (C=O), 1377, 1265, 1125, 895, 830, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.71 (s, 3 H, OMe), 3.20 (s, 3 H, NMe), 3.88 (br s, 1 H, OH), 5.62 (d, 1 H, J = 7.2 Hz, 6-H), 6.23 (d, 1 H, J = 7.2 Hz, 5-H).

2-Ethyl-2-hydroxy-4-methyl-2*H*-1,4-thiazin-3(4*H*)-one (5i). Diketone **4a** (217 mg, 1.52 mmol) was treated with a Grignard reagent made from ethyl bromide (497 mg, 4.56 mmol) and magnesium (110 mg, 4.53 mmol) in THF to yield 195 mg (74%) of crude **5i** as a brown oil. Chromatography on silica gel (benzene–ethyl acetate, 8:2) gave 124 mg (47%) of pure **5i** as a yellow oil: IR (neat) 3350 (OH), 1640 (C=O), 1377, 1252, 1172, 875, 700

(10) DeStevens, G.; Halamandaris, A.; Dorfman, L. *J. Am. Chem. Soc.* **1958**, *80*, 5198.

cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (t, 3 H, J = 7.8 Hz, CMe), 1.96 (q, 2 H, J = 7.8 Hz, CH_2), 3.20 (s, 3 H, NMe), 3.84 (br s, 1 H, OH), 5.59 (d, 1 H, J = 7.2 Hz, 6-H), 6.18 (d, 1 H, J = 7.2 Hz, 5-H).

2-*tert*-Butyl-2-hydroxy-4-methyl-2*H*-1,4-thiazin-3(4*H*)-one (5j). To a Grignard reagent made from *tert*-butyl chloride (2.02 g, 21.8 mmol) and magnesium (617 mg, 25.4 mmol) in THF (30 mL) was added dropwise diketone **4a** (1.04 g, 7.27 mmol) in THF (20 mL) in an ice bath, and the reaction mixture was stirred for 3 h at room temperature. After the usual workup, 1.18 g of crude oil was chromatographed on silica gel (benzene–ethyl acetate, 19:1) to yield **5j** (500 mg, 34.1%) as light brown crystals. Recrystallization from hexane–chloroform gave white crystals: mp 80–81 °C; UV (MeOH) 290 (ε 2400) nm; IR (KBr) 3350 (OH), 2958, 1617 (C=O), 1360, 1258, 1228, 1125, 1067, 894, 793, 683 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 9 H, CMe), 3.18 (s, 3 H, NMe), 4.38 (br s, 1 H, OH), 5.46 (d, 1 H, J = 7.2 Hz, 6-H), 6.00 (d, 1 H, J = 7.2 Hz, 5-H). Anal. Calcd for $C_9H_{15}NO_2S$: C, 53.70; H, 7.51; N, 6.96; S, 15.93. Found: C, 53.48; H, 7.46; N, 6.69; S, 16.03.

Nucleophilic Reaction of the Cation 6 with Methanol. A solution of the cation **6e** prepared by dissolving 2-(*p*-methoxyphenyl) alcohol **5e** (23 mg, 0.91 mmol) in TFA (2 mL) was poured into methanol (10 mL). After being stirred for 0.5 h at room temperature, the reaction mixture was poured into water and extracted with CH_2Cl_2, washed with water, and dried (Na_2SO_4). Evaporation of the solvent gave raw product (240 mg, 93%). Chromatography on silica gel (benzene–ethyl acetate, 8:2) yielded light brown crystals (170 mg, 66%). Recrystallization from chloroform–hexane afforded pure ether **8e** as white crystals: mp 110 °C; IR (KBr) 1662 (C=O), 1610, 1514, 1370, 1300, 1266, 1178, 868, 830, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.20 (s, 3 H, NMe or 2-OMe), 3.23 (s, 3 H, 2-OMe or NMe), 3.76 (s, 3 H, para OMe), 5.53 (d, 1 H, J = 7.2 Hz, 6-H), 6.33 (d, 1 H, J = 7.2 Hz, 5-H), 7.02 (d, 2 H, J = 8.4 Hz, 3′-H), 7.36 (d, 2 H, J = 8.4 Hz, 2′-H). Anal. Calcd for $C_{13}H_{15}O_3NS$: C, 58.85; H, 5.70; N, 5.28; S, 12.08. Found: C, 58.31; H, 5.64; N, 5.02; S, 11.84.

8a: oil; ^1H NMR ($CDCl_3$) δ 3.20 (s, 3 H, NMe), 3.24 (s, 3 H, OMe), 5.56 (d, 1 H, J = 7.2 Hz, 6-H), 6.36 (d, 1 H, J = 7.2 Hz, 5-H), 7.10–7.64 (m, 5 H, Ph).

8k: oil; IR (neat) 1665 (C=O), 1510, 1365, 1255, 1175, 1030, 807, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03 (s, 3 H, SMe), 3.22 (s, 3 H, NMe), 3.78 (s, 3 H, OMe), 5.49 (d, 1 H, J = 7.2 Hz, 6-H), 6.14 (d, 1 H, J = 7.2 Hz, 5-H), 6.97 (d, 2 H, J = 9.0 Hz, 3′-H), 7.51 (d, 2 H, J = 9.0 Hz, 2′-H).

2-(*p*-Methoxyphenyl)-4-methyl-3-oxo-3,4-dihydro-2*H*-1,4-thiazin-2-ylium Tetrafluoroborate (9e) [3-(*p*-Methoxyphenyl)-1-methyl-2-oxido-4-thioniapyridinium Tetrafluoroborate]. To an ice-cold solution of 2-hydroxy-2-(*p*-methoxyphenyl)-4-methyl-2*H*-1,4-thiazin-3(4*H*)-one (**5e**) (593 mg, 2.36 mmol) in propionic anhydride (7 mL) was added dropwise a mixture of 994 mg of 42% tetrafluoroboric acid (417 mg, 4.75 mmol of HBF_4) and propionic anhydride (7 mL). On addition of the acid the colorless solution turned to purple. After the mixture was stirred for a few minutes, diethyl ether (20 mL) was added to the reaction mixture to precipitate the salt **9e** (641 mg, 85%) as purple crystals. Recrystallization from ether–acetonitrile gave pure salt: mp 70 °C dec; IR (KBr) 1647 (C=O), 1608, 1510, 1255, 1080 (BF_4^-), 1035 (BF_4^-) cm^{-1}; ^1H NMR (CD_3NO_2) δ 3.87 (s, 3 H, NMe), 4.03 (s, 3 H, OMe), 7.17 (d, 2 H, J = 9.0 Hz, 3′-H), 7.58 (d, 1 H, 7.8 Hz, 6-H), 8.16–8.52 (m, 3 H, 2′-H and 5-H). Anal. Calcd for $C_{12}H_{12}O_2NSBF_4$: C, 44.89; H, 3.77; N, 4.36. Found: C, 44.90; H, 3.71; N, 4.35.

4-Methyl-3-oxo-2-*p*-tolyl-3,4-dihydro-2*H*-1,4-thiazin-2-ylium Tetrafluoroborate (9d) [1-Methyl-2-oxido-3-*p*-tolyl-4-thioniapyridinium Tetrafluoroborate]. 2-Hydroxy-4-methyl-2-*p*-tolyl-2*H*-1,4-thiazin-3(4*H*)-one (**5d**) (250 mg, 1.13 mmol) and 42% HBF_4 (473 mg, 2.26 mmol) gave the tetrafluoroborate (163 mg, 52%) as red crystals: mp 72 °C dec (ether–acetonitrile); IR (KBr) 1640 (C=O), 1513, 1380, 1256, 1084, 1067 (BF_4^-), 1037 (BF_4^-), 815 cm^{-1}; ^1H NMR (CD_3NO_2) δ 2.48 (s, 3 H, para Me), 3.87 (s, 3 H, NMe), 7.43 (d, 2 H, J = 9.0 Hz, 3′-H), 7.78 (d, 1 H, J = 7.8 Hz, 6-H), 8.06 (d, 2 H, J = 9.0 Hz, 2′-H), 8.60 (d, 1 H, J = 7.8 Hz, 5-H). Anal. Calcd for $C_{12}H_{12}ONSBF_4$: C, 47.24; H, 3.96; N, 4.60. Found: C, 46.32; H, 3.72; N, 4.42.

4,5-Dimethyl-3-oxo-2-phenyl-3,4-dihydro-2*H*-1,4-thiazin-2-ylium Tetrafluoroborate (9f) [1,6-Dimethyl-2-oxido-3-phenyl-4-thioniapyridinium Tetrafluoroborate]. Alcohol **5f** (100 mg, 0.425 mmol) and 42% HBF_4 (176 mg, 0.85 mmol) gave **9f** (70 mg, 54%) as orange crystals: mp 70–71 °C (ether–acetonitrile); IR (KBr) 1670 (C=O), 1595, 1450, 1310, 1225, 1085 (BF_4^-), 1040 (BF_4^-), 750, 700 cm^{-1}; ^1H NMR (CD_3NO_2) δ 2.85 (s, 3 H, 5-Me), 3.86 (s, 3 H, NMe), 7.76 (s, 1 H, 6-H), 7.29–8.18 (m, 5 H, Ph). Anal. Calcd for $C_{12}H_{12}ONSBF_4$: C, 47.24; H, 3.96; N, 4.59. Found: C, 46.64; H, 4.22; N, 4.65.

2-*tert*-Butyl-4-methyl-3-oxo-3,4-dihydro-2*H*-1,4-thiazin-2-ylium Tetrafluoroborate (9j) [3-*tert*-Butyl-1-methyl-2-oxido-4-thioniapyridinium Tetrafluoroborate]. 2-*tert*-Butyl-2-hydroxy-4-methyl-2*H*-1,4-thiazin-3(4*H*)-one (**5j**) (186 mg, 0.92 mmol) and 42% HBF_4 (385 mg, 1.84 mmol) gave the tetrafluoroborate (170 mg, 68%) as yellow crystals. This salt is so hygroscopic that its melting point and IR spectrum cannot be observed successfully: ^1H NMR (CD_3NO_2) δ 8.46 (d, 1 H, J = 7.2 Hz, 5-H), 7.76 (d, 1 H, J = 7.2 Hz, 6-H), 3.81 (s, 3 H, NMe), 1.62 (s, 9 H, *t*-Bu); UV–vis spectrum (CH_2Cl_2) 415 nm.

Registry No. 1 (3,4-dimethyl deriv.), 35990-82-0; **4a**, 82409-29-8; **4b**, 113925-45-4; **4b** (2-(dimethyl acetal)), 113925-44-3; **5a**, 113925-46-5; **5b**, 113925-47-6; **5c**, 113925-48-7; **5d**, 113925-49-8; **5e**, 113925-50-1; **5f**, 113925-51-2; **5g**, 113925-52-3; **5h**, 113925-53-4; **5i**, 113925-54-5; **5j**, 113925-55-6; **6a**, 113925-68-1; **6b**, 113925-70-5; **6c**, 113925-72-7; **6d**, 113925-73-8; **6e**, 113925-74-9; **6f**, 113925-75-0; **6g**, 113925-78-3; **6j**, 113925-76-1; **8a**, 113925-57-8; **8e**, 113925-56-7; **8k**, 113925-58-9; **9d**, 113925-62-5; **9e**, 113925-60-3; **9f**, 113925-64-7; **9j**, 113925-66-9; $ClCH_2COCH_3$, 78-95-5; $CH_3C(=S)NH_2$, 62-55-5; PhBr, 108-86-1; *p*-FC_6H_4Br, 460-00-4; *p*-ClC_6H_4Br, 106-39-8; *p*-MeC_6H_4Br, 106-38-7; *p*-$MeOC_6H_4Br$, 104-92-7; 2,4-dimethylthiazole, 541-58-2; 2,3,4-trimethylthiazolium iodide, 5787-82-6; 2-(iodomethyl)-3,4-dimethylthiazolium iodide, 113925-43-2.

Supplementary Material Available: ^{13}C NMR data for alcohols **5** (1 page). Ordering information is given on any current masthead page.