15l, 104507-69-9; **15m**, 104507-70-2; **16**, 104507-95-1; (*E*)-**17**, 104488-74-6; (*Z*)-**17**, 104488-75-7; (*E*)-**18**, 104507-77-9; (*Z*)-**18**, 104507-78-0; (*E*)-**19**, 104488-90-6; (*Z*)-**19**, 104488-91-7; (*E*)-**20**, 104488-92-8; (*Z*)-**20**, 104488-93-9; **21a**, 104507-79-1; **21d**, 104507-85-9; **21f**, 104507-89-3; **21g**, 104507-92-8; (*E*)-**22a**, 104507-80-4; (*Z*)-**22a**, 104507-81-5; (*E*)-**22b**, 104507-82-6; (*Z*)-**22b**, 104507-83-7; **22c**, 104507-84-8; (*E*)-**22d**, 104507-86-0; (*E*)-**22e**, 104507-87-1; (*Z*)-**22e**, 104507-88-2; (*E*)-**22f**, 104507-90-6; (*Z*)-**22f**, 104507-91-7; (*E*)-**22g**, 104507-93-9; (*Z*)-**22g**, 104507-94-0; **23a**, 93548-39-1; **23b**, 93548-42-6; **23c**, 93548-43-7; **23f**, 93548-47-1; **23g**, 61862-37-1; **24e**, 104507-96-2; **25**, 89103-82-2; **25** (ketone), 1624-62-0; **26**, 104531-39-7; **27**, 91940-11-3; (*E*)-**28**, 56691-80-6; (*Z*)-**28**, 56881-52-8; **29**, 54897-36-8; **30**, 72863-24-2; **31**, 96921-49-2; **32**, 104507-97-3; **33**, 104507-98-4; **34a**, 98810-10-7; **34b**, 100229-88-7; **34c**, 104508-00-1; **34d**, 104508-01-2; **35b**, 104507-99-5; (*E*)-**36**, 104488-82-6; (*Z*)-**36**, 104488-83-7; (*E*)-**37**, 104488-86-0; (*Z*)-**37**, 104488-87-1; **38a**, 104508-02-3; **38b**, 84602-97-1; **38c**, 104508-06-7; **38d**, 104508-09-0; (*E*)-**39a**, 104508-03-4; (*Z*)-**39a**, 104531-55-7; (*E*)-**39b**, 104508-04-5; (*Z*)-39b, 104508-05-6; (*E*)-**39c**, 104508-07-8; (*Z*)-**39c**, 104508-08-9; (*E*)-**39d**, 104508-10-3; (*Z*)-**39d**, 104508-11-4; **40a**, 97663-40-6; **40b**, 97663-36-0; **40c**, 97663-37-1; **40d**, 82234-80-8; **40e**, 87413-32-9; **40f**, 49639-05-6; **41c**, 97663-38-2; **41d**, 104508-12-5; DPPE, 1663-45-2; Pd(dba)$_2$, 33677-55-3: MeC(NO$_2$)=CHMe, 4812-23-1; H_2C=CHCO$_2$Me, 96-33-3; H_2C=CHAc, 78-94-4; Pd(PPh$_3$)$_4$, 14221-01-3; PPh$_3$, 603-35-0; MeNO$_2$, 75-52-5; Me$_2$N(CH$_2$)$_2$NH$_2$, 108-00-9; PhSO$_2$Na, 873-55-2; NaNO$_2$, 7632-00-0; PhSO$_2$CH$_2$CH=CHCH$_2$OAc, 95177-57-4; EtCH=C(Me)NO$_2$, 6065-19-6; EtC(NO$_2$)=CHPr, 6187-24-2; EtCH=C(Et)NO$_2$, 4812-22-0; MeC(NO$_2$)=CHPr, 6065-17-4; MeC(NO$_2$)=CH(CH$_2$)$_3$Pr, 4812-25-3; EtC(NO$_2$)=CHMe, 6065-18-5; H_2C=CHCH(Me)OAc, 6737-11-7; (*E*)-MeCH=CHCH$_2$OAc, 7204-29-7; (*E*)-PhCH=CHCH$_2$OAc, 21040-45-9; (*E*)-PhCH=CHCH$_2$SO$_2$Ph, 16212-07-0; (*Z*)-AcOCH$_2$CH=CHCH$_2$OAc, 25260-60-0; (*E*)-PhSO$_2$CH$_2$CH=CHCH$_2$SO$_2$Ph, 62384-73-0; Me$_2$C=CHNO$_2$, 1606-30-0; 1-(nitromethyl)-3,4-dihydronaphthalene, 104489-04-5; 1-nitrocyclohexene, 2562-37-0; 1-nitrocycloheptene, 36291-53-9; linalyl acetate, 115-95-7; 1-((phenylsulfonyl)methyl)cyclohexene. 49639-03-4; 3-methyl-2-(nitromethyl)cyclohexene, 104489-00-1.

Quantitative Comparison of the Heteroatom Effects in the Methoxide Attachment to Pyrylium and Thiopyrylium Cations. Thermodynamics of the Isomerization of Pyrans and Thiopyrans

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The complete set of kinetic and equilibrium constants for the methoxide attachment to a series of 2,6-di-*tert*-butyl-4-arylpyrylium cations (aryl = XC_6H_4 with X = *p*-NO$_2$, *m*-Cl, *p*-Cl, H, *p*-Me, *p*-OMe, *p*-NMe$_2$) has been obtained in MeOH at 25 °C. These data complement those previously obtained by studying the methoxide attachment to the corresponding thiopyrylium cations. In both series the reaction involves the kinetically controlled formation of both the corresponding 2*H* and 4*H* adducts which equilibrate to form only the thermodynamically more stable 2*H* adduct. The observed kinetic patterns show that the rate-determining step is the combination of the nucleophile with the cation to give the adducts. Moreover, the experimental data indicate that the Leffler–Hammond postulate cannot give information on the position of the transition state along the reaction coordinate. Both kinetic and equilibrium constants for the formation of the 2*H* and 4*H* adducts are correlated with the σ^+ constants. The obtained ρ values show, for the pyrylium series, a greater sensitivity to the substituent effects with respect to the corresponding thiopyrylium series. From the equilibrium data we estimate that, in contrast with quantum mechanical calculations, the unsubstituted 2*H*-pyran is at least 4.6 kcal/mol more stable than the corresponding 4*H* isomer.

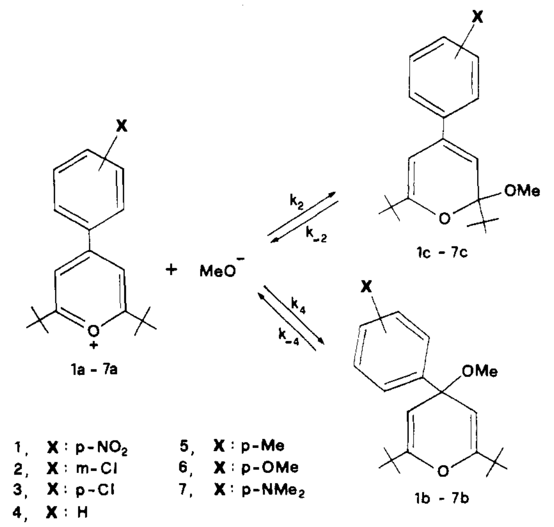
The chemistry of the ambident heteroaromatic cations, pyridinium, pyrylium, and thiopyrylium, presents a number of stimulating problems that attract the attention of the physical organic chemist. In particular, the reactivity of these cations with nucleophilic reagents can give valuable information about important topics, such as ring heteroatom effects, anion–cation combination reactions, and theoretical approaches to regioselectivity.

Here we wish to report a detailed kinetic and thermodynamic study of the methoxide attachment to 2,6-di-*tert*-butyl-4-arylpyrylium cations **1a–7a** in methanol at 25 °C to yield the corresponding 4*H*- (**1b–7b**) and 2*H*-pyrans (**1c–7c**).

These data complement those previously obtained by studying the methoxide attachment to the corresponding thiopyrylium cations 8–14 in methanol at 25 °C.[1]

Our aim is to assess in a quantitative and systematic way the role of the heteroatom on the electrophilic behavior of such ambident cations.

Scheme I



Results

^{1}H NMR Study. The ^{1}H NMR study of the reaction was performed at −30 °C and 30 °C, respectively.

The experiments carried out at −30 °C, with an excess of CD_3O^- in CD_3OD, lead to the immediate disappearance of the signals of the substrates and the appearance at

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[1] Di Vona, M. L.; Doddi, G.; Ercolani, G.; Illuminati, G. *J. Am. Chem. Soc.* **1986**, *108*, 3409.

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higher fields, owing to the neutralization of the positive charge, of the signals of the corresponding 2*H* and 4*H* adducts (Scheme I).

At variance, the compound **7a** shows the formation of only the 2*H* adduct **7c**.

Since in the case of cation **1a** isomer equilibration is very slow, the composition of the reaction mixture is kinetically controlled. Under this condition the molar ratio **1c**/**1b**, as measured by NMR (0.22) coincides with the corresponding k_2/k_4 ratio. On raising the temperature to 30 °C, the complete conversion of the 4*H* adducts **1b**–**6b** to the 2*H* isomers **1c**–**6c** is observed.

The ^1H NMR data are reported in the Experimental Section.

Kinetic and Equilibrium Measurements. The kinetic experiments were carried out in methanol at 25.0 °C, under pseudo-first-order conditions, in a stopped-flow spectrophotometer, by mixing the substrates **1a**–**7a** (1–3 $\times$ 10^{-5} M after mixing) with a large excess of sodium methoxide ((2×10^{-4}) – (2×10^{-3}) M after mixing) and/or Et_3N/Et_3NH^+ buffers (yielding [MeO^-] $\sim$ (1×10^{-7}) – (6×10^{-6}) M after mixing), depending on the reactivity of the substrate. In all the kinetic experiments carried out with Et_3N/Et_3NH^+ buffers we had no evidence of general acid–base buffer catalysis. The reaction was monitored at two wavelengths: λ_A, where only the substrate absorbs, and λ_B, where both the substrate and the corresponding 2*H* adduct absorb (see Experimental Section for λ_A and λ_B values). The only exception was cation **1a** whose kinetics were followed at only one wavelength because it absorbs in the same region as that of corresponding 2*H* and 4*H* adducts.

The observed kinetic patterns are fully consistent with the mechanism depicted in Scheme I for which the following equations hold:[2]

$$\tau_1^{-1} + \tau_2^{-1} = (k_2 + k_4)[MeO^-] + k_{-2} + k_{-4} \qquad (1)$$

$$\tau_1^{-1} \times \tau_2^{-1} = (k_2 k_{-4} + k_4 k_{-2})[MeO^-] + k_{-2}\, k_{-4} \qquad (2)$$

where τ_1 and τ_2 are the relaxation times of the two observed first-order processes. Considering that the equilibrium in the conditions of the kinetic experiments is always completely shifted toward the 2*H* adduct, eq 1 and 2 reduce to

$$\tau_1^{-1} + \tau_2^{-1} = (k_2 + k_4)[MeO^-] + k_{-4} \qquad (3)$$

$$\tau_1^{-1} \times \tau_2^{-1} = k_2[MeO^-] \times k_{-4} \qquad (4)$$

Three kinetic patterns were observed, depending on the reactivity of the cation and on the methoxide ion concentration: (i) the two processes are widely separated, hence, eq 3 and 4 can be simplified as follows:

$$\tau_1^{-1} = (k_2 + k_4)[MeO^-] \qquad (5)$$

$$\tau_2^{-1} = \frac{k_2\, k_{-4}}{k_2 + k_4} \qquad (6)$$

(ii) the two processes are not widely separated, and then eq 3 and 4 hold; (iii) only one process is observed ($k_{-4} \gg k_4[MeO^-]$) which refers only to the formation of the 2*H* adduct:

$$\tau^{-1} = k_2[MeO^-] \qquad (7)$$

The evaluation of the kinetic constants was accomplished as follows: (a) Cation **1a**, in the range of [MeO^-] $\sim$ (1×10^{-7}) – (1×10^{-6}) M, shows the kinetic pattern i characterized by eq 5 and 6, from which the values of ($k_2 + k_4$) and $k_2\, k_{-4}$ can be obtained (Table S1). Assuming that the ratio k_2/k_4 does not change appreciably with the temperature,[3] the k_2/k_4 value measured by NMR at –30 °C permits the evaluation of k_2, k_4, k_{-4}, and the equilibrium constant K_4 ($= k_4/k_{-4}$). Unfortunately the k_2/k_4 ratio could not be determined spectrophotometrically at 25 °C as for the cations **2a**–**4a** (vide infra), because the 4*H* adduct **1b** absorbs in the same region as that of the 2*H* isomer **1c**.

(b) Cations **2a**–**4a**, in the range of [MeO^-] $\sim$ (4×10^{-7}) – (6×10^{-6}) M follow the kinetic pattern ii characterized by eq 3 and 4 (Tables S2–S4). Plotting ($\tau_1^{-1} + \tau_2^{-1}$) vs. [$MeO^-$] and ($\tau_1^{-1} \times \tau_2^{-1}$) vs. [$MeO^-$], straight lines are obtained whose slopes are ($k_2 + k_4$) and $k_2\, k_{-4}$, respectively. Actually the intercept of the first plot should give the k_{-4} constant; however, since this term in our experimental conditions is generally small, its determination is affected by a large error, and therefore the value of the intercept was not taken into account for the k_{-4} determination. In order to obtain the individual values of the constants, we found it convenient to determine spectrophotometrically the k_2/k_4 ratio at [MeO^-] $\sim$ 2×10^{-3} M, according to a procedure previously described.[1]

(c) Cations **5a** and **6a**, in the range of [MeO^-] $\sim$ (3×10^{-4}) – (1.5×10^{-3}) M show the kinetic pattern i and, therefore, from eq 5 and 6 the values of ($k_2 + k_4$) and $k_2 k_{-4}$ are obtained (Tables S6, S8). Kinetic experiments carried out in the range of [MeO^-] $\sim$ (1×10^{-7}) – (1×10^{-6}) M (Tables S5, S7) show only one process from which k_2 is obtained (eq 7), thus permitting also the evaluation of the k_4, k_{-4}, and K_4 constants. It is worth remarking that k_2/k_4 ratios obtained spectrophotometrically are in nice agreement with those calculated from k_2 and k_4.

(d) Cation **7a** in the range of [MeO^-] $\sim$ (2×10^{-4}) – (2×10^{-3}) M shows only the formation of the 2*H*-pyran **7c** (Table S9), in accordance with the NMR observations. From these data only the k_2 constant can be evaluated (eq 7). The k_4, k_{-4}, and K_4 values were not experimentally accessible also at high methoxide concentrations (10^{-2} – 10^{-1} M). An estimation of these values, assuming a similar behavior of the pyrylium and thiopyrylium series, can be accomplished by extrapolation from the linear plots log k_4(pyrylium) vs. log k_4(thiopyrylium) (plot not shown; $r = 0.997$), and log K_4(pyrylium) vs. log K_4 (thiopyrylium) (plot not shown; $r = 0.999$). The estimated values of k_4 and K_4 are consistent with their experimental inaccessibility.

The equilibrium constants K_2 were obtained spectrometrically at very low methoxide concentrations, with buffer solutions. Under these conditions the cations **1a**–**7a** are only partially converted into the corresponding 2*H* adducts, thus permitting the determination of the equilibrium constants K_2. Further details are reported in the Experimental Section.

From the K_2 and k_2 values the kinetic constants k_{-2} ($= k_2/K_2$) can be calculated.

The kinetic and equilibrium constants for the reactions of pyrylium cations **1a**–**7a** are reported in Table I. Table II shows a summary of the kinetic and equilibrium constants for the corresponding thiopyrylium cations **8**–**14**, obtained in our previous work.[1] In both series the con-

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[2] For an exhaustive treatment of relaxation kinetics, see: Bernasconi, C. F. *Relaxation Kinetics*; Academic Press: New York, 1976.

[3] (a) This assumption is based on kinetic investigations carried out at 25 °C for 2,4,6-triphenylthiopyrylium[3b] and for 2,6-di-*tert*-butyl-4-phenylthiopyrylium,[1] which afforded k_4/k_2 values (1.4 and 4.5, respectively), in good agreement with the molar ratios 4*H*/2*H* obtained by ^1H NMR at –40 °C (1.5 and 4.6, respectively).[3c] (b) Doddi, G.; Illuminati, G.; Insam, N.; Stegel, F. *J. Org. Chem.* **1982**, *47*, 960. (c) Doddi, G.; Ercolani, G. *J. Chem. Soc., Perkin Trans. 2* **1986**, 271.

Table I. Rates and Equilibrium Constants for the Reaction of Pyrylium Ions 1a–7a with MeO$^-$, in Methanol, at 25.0 °C

cation	k_4, s^{-1} M^{-1}	k_{-4}, s^{-1}	K_4, M^{-1}	k_2,^{a} s^{-1} M^{-1}	k_{-2}, s^{-1}	K_2,^{a} M^{-1}
1a	$1.5 \times 10^{7\,b}$	$1.0 \times 10^{-1\,b}$	$1.4 \times 10^{8\,b}$	$3.3 \times 10^{6\,b}$	$1.5 \times 10^{-6\,b}$	2.2×10^{12}
2a	4.0×10^{6}	3.3×10^{-1}	1.2×10^{7}	1.4×10^{6}	1.4×10^{-5}	1.0×10^{11}
3a	3.2×10^{6}	9.1×10^{-1}	3.5×10^{6}	8.4×10^{5}	1.9×10^{-5}	4.3×10^{10}
4a	$1.3_5 \times 10^{6}$	2.7	5.1×10^{5}	3.5×10^{5}	2.9×10^{-5}	1.2×10^{10}
5a	$8.1_5 \times 10^{5}$	6.3	1.3×10^{5}	2.1×10^{5}	6.9×10^{-5}	3.1×10^{9}
6a	3.2×10^{5}	13	2.5×10^{4}	9.9×10^{4}	2.1×10^{-4}	4.8×10^{8}
7a	$1.1 \times 10^{4\,c}$	$6.9 \times 10^{2\,c}$	16^{c}	1.4×10^{3}	2.9×10^{-3}	4.8×10^{5}

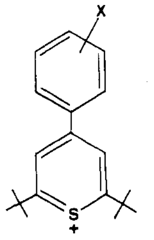
[a] Not corrected for the statistical factor. [b] Estimated by the assumption $(k_2/k_4)_{-30\,°C} = (k_2/k_4)_{25\,°C}$, see text. [c] Estimated value, see text.

Table II. Rates and Equilibrium Constants for the Reaction of Thiopyrylium Ions 8–14 with MeO$^-$, in Methanol, at 25.0 °C^a

cation	k_4, s^{-1} M^{-1}	K_4, M^{-1}	k_2,^{b} s^{-1} M^{-1}	K_2,^{b} M^{-1}
8	4.0×10^{5}	6.4×10^{6}	5.2×10^{4}	1.1×10^{9}
9	1.5×10^{5}	9.2×10^{5}	2.5×10^{4}	$1.2_5 \times 10^{8}$
10	1.0×10^{5}	3.3×10^{5}	1.8×10^{4}	6.4×10^{7}
11	5.4×10^{4}	8.5×10^{4}	1.2×10^{4}	1.6×10^{7}
12	3.1×10^{4}	2.4×10^{4}	7.4×10^{3}	6.6×10^{6}
13	1.7×10^{4}	9.9×10^{3}	4.8×10^{3}	1.7×10^{6}
14	9×10^{2}	3×10	7.5×10	7.9×10^{3}

[a] From ref 1. [b] Not corrected for the statistical factor.

stants k_2 and K_2 were not corrected for the statistical factor.



8–14

8, X : p-NO$_2$
9, X : m-Cl
10, X : p-Cl
11, X : H
12, X : p-Me
13, X : p-OMe
14, X : p-NMe$_2$

Discussion

Mechanistic Features. Apart from the cation **7a** whose 4*H* adduct **7b** was not detected, the cations **1a**–**6a** show a similar reaction mechanism, i.e., the kinetically controlled formation of both the corresponding 2*H*- and 4*H*-pyrans which equilibrate to form only the thermodynamically more stable 2*H*-pyran. Although the 4*H*-pyran **7b** was not detected, the estimated kinetic and equilibrium constants for its formation accord with the above mechanism. The same mechanistic features were observed for the reaction of the thiopyrylium series **8**–**14**.[1] In our previous work[1] we have shown that the occurrence of the kinetic pattern ii rules out a reaction mechanism, alternative to that shown in Scheme I, involving the rate-determining formation of a common species, such as an ion pair or a donor–acceptor complex, preceding the formation of 2*H* and 4*H* adducts. At variance the kinetic pattern ii indicates that in these reactions there are two rate-determining transition states in which the nucleophile and each electrophilic center specifically interact.

In a recent paper[4] Gandler has proposed, following earlier indications of Ritchie,[5] that the reaction of hydroxide ion in water with some triarylmethyl cations follows either a concerted or a preassociation mechanism involving the assisted attachment of a water molecule in the transition state. At variance, with other preformed cations, such as tropylium[6a] and diferrocenylmethyl[6b] ions, a direct nucleophilic attack of hydroxide ion was envisaged. By analogy also for the methoxide attachment in methanol there are these mechanistic alternatives.[7] However, since we have not observed general base catalysis with triethylamine, it seems more likely that, with pyrylium cations, methoxide would act as a normal nucleophile. It should be pointed out, however, that even though the other mechanisms would operate, our previous mechanistic conclusion would not be invalidated. Only the nature of the two rate-determining transition states should be reconsidered.

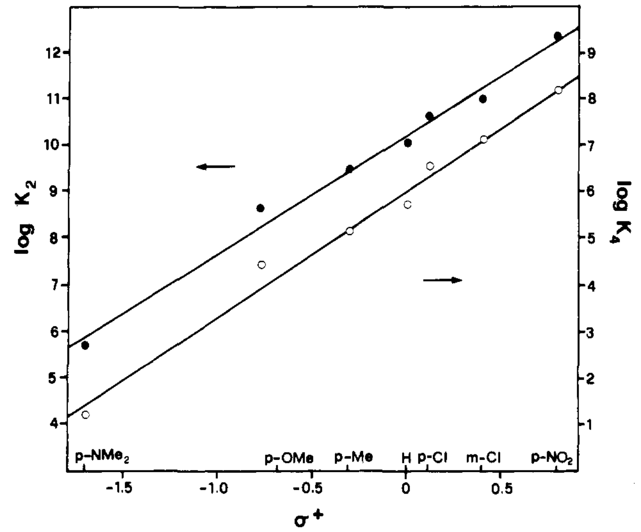


Figure 1. Equilibrium–σ^+ relationships for the formation of 2*H*- (●) and 4*H*- (○) pyrans.

Substituent and Heteroatom Effects. Figure 1 shows the correlations between the equilibrium constants K_2 and K_4 with respect to σ^+ values ($\rho_2^{eq} = 2.6$, $r = 0.994$; $\rho_4^{eq} = 2.7$, $r = 0.993$). The better correlations of the equilibrium constants with σ^+ than with σ values (plots not shown) indicate a normal transmission of resonance effects with the positively charged pyrylium ring, despite the fact that X-ray investigations on a related compound, viz. 2,4,6-triphenylpyrylium, have shown a twisting of the γ-phenyl group with respect to the mean plane of the heteroaromatic ring, ranging from ~18° to ~29°, depending on the counterion.[8] The similarity of ρ_2^{eq} and ρ_4^{eq} is not surprising, because the substituents are expected to affect much more the standard free energy of the starting cation

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(4) Gandler, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 8218.

(5) Ritchie, C. D. *J. Am. Chem. Soc.* **1972**, *94*, 3275.

(6) (a) Bunton, C. A.; Davoudzadeh, F.; Watts, W. E. *J. Am. Chem. Soc.* **1981**, *101*, 3855. (b) Bunton, C. A.; Carrasco, N.; Davoudzadeh, F.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1520.

(7) A direct nucleophilic attack of alkoxide ions on phthalimidium cation in water–alcohol mixtures for the uncatalyzed reactions has been reported: Gravitz, N.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 507.

(8) (a) Tamamura, T.; Yamane, T.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 832. (b) Bokii, N. G.; Vedrinskii, R. V.; Kitaev, V. V.; Lopatina, N. A.; Struchkov, Yu. T. *Koord. Khim.* **1976**, *2*, 103. (c) Kompan, O. E.; Potekhin, K. A.; Furmanova; N. G.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1980**, *21*, 194.

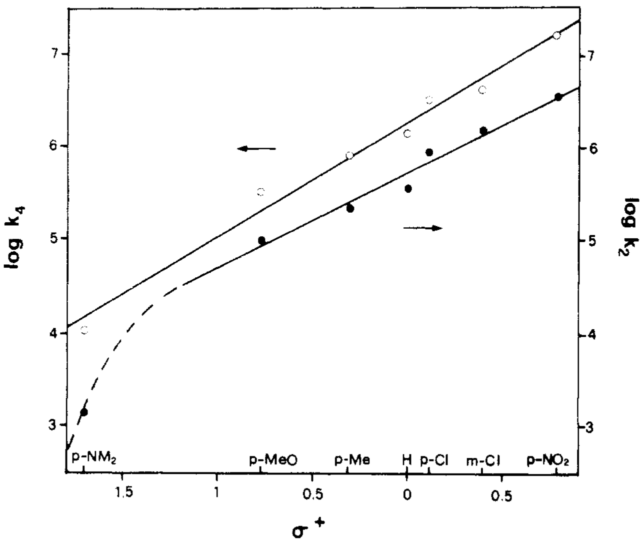

Figure 2. Rate–σ^+ relationships for the formation of 2*H*- (●) and 4*H*- (○) pyrans.

than that of the corresponding neutral adducts. It is interesting to compare the above reported ρ^{eq} values with those obtained for the thiopyrylium series ($\rho_2^{eq} = 2.0$; $\rho_4^{eq} = 2.1$).[1] The moderately higher ρ^{eq} values for the pyrylium series show that the partial positive charge, as seen by the substituents, is greater in the pyrylium than in the thiopyrylium ring. Different charge densities on the two rings are also suggested by the higher reactivity of each pyrylium cation with respect to the corresponding thiopyrylium one. This result is in accordance with nonempirical calculations of Palmer et al.,[9] indicating that the α and γ carbon atoms of the pyrylium ring have a higher charge density with respect to those of the thiopyrylium cation. These calculations show that also the difference between the charge density of the α and γ carbon atoms is higher for the pyrylium cation. This result accounts for the different regioselectivity of methoxide ion in the two heteroaromatic systems, with the ratio k_2/k_4 for each pyrylium cation higher than that for the corresponding sulfur analogue. Ritchie pointed out that the selectivity for anion–cation combination reactions is independent from the charge of the nucleophile and on this basis ruled out the operation of Coulombic effects.[10] However, we wish to remark that the positive charge density of a given electrophilic site is a main factor in determining its reactivity with a given nucleophile. This can be shown by the positive ρ values obtained for the reactivity of cation series with a given nucleophile[1,11,12] and, as above indicated, by the higher reactivity of pyrylium cations with respect to the corresponding thiopyrylium ones (see also ref 3b).

As shown in Figure 2, also the kinetic constants k_2 (with the exception of **7a**) and k_4 are linearly correlated with positive slopes by the σ^+ values ($\rho_2^{kin} = 1.0$, $r = 0.984$; $\rho_4^{kin} = 1.2$, $r = 0.991$). The order $\rho_4^{kin} > \rho_2^{kin}$ can be ascribed to the different transmission efficiencies[13] of electronic effects between the substituent and the two reactive centers. In fact, while the α position interacts with the substituent through the heteroaromatic ring, the γ position directly interacts with the substituted phenyl group. Deviations of the dimethylamino group, analogous with that shown by the log k_2–σ^+ plot, were already observed in the thiopyrylium and tropylium series,[1] thus suggesting that this is a general feature of positively charged aromatic systems. The dimethylamino group probably alters the transmission efficiencies of these particular π systems because of the strong resonance interactions.

The ρ^{kin} and ρ^{eq} values permit the calculation of the α_2 ($= \rho_2^{kin}/\rho_2^{eq} = 0.38$) and α_4 ($= \rho_4^{kin}/\rho_4^{eq} = 0.44$) parameters. The α parameter is usually interpreted in terms of position of the transition state along the reaction coordinate.[14] This interpretation relies on the assumption that in a reaction series, the variations of the activation barrier are only a fraction of the variations of the thermodynamics of the reaction. However, this interpretation must be abandoned in our case, because the observation of a kinetic control different from a thermodynamic one points to the importance of additional factors which are present in the transition state but absent in reactants or products.[1,15]

These additional factors that could be regarded as kinetic factors are also evidenced by the breakdown of the reactivity–selectivity principle.[14,15] In fact, in spite of the higher reactivity of each pyrylium cation with respect to the corresponding thiopyrylium one, the ρ^{kin} values of the former series are not lower than the corresponding values of the latter ($\rho_2^{kin} = 0.67$; $\rho_4^{kin} = 1.0$),[1] as would be expected on the basis of the reactivity–selectivity principle. The failure of this principle in anion–cation combination reactions, although in a different context, is well-known, being the principal feature of the constant selectivity N_+ relationship.[10] The additional contribution to the Gibbs energy of activation can be ascribed to the desolvation and interaction of the ions. The electronic substituent effects, modifying the charge density of the electrophilic site, are expected to affect such kinetic barrier. Therefore, this fact makes the Leffler–Hammond postulate no longer valid, and the α value no longer indicative of the position of the transition state along the reaction coordinate. It should be pointed out that the observation of a linear rate–equilibrium correlation is not a sufficient condition to justify the validity of the Leffler–Hammond postulate in a given reaction series. In fact, if there are kinetic factors which are linearly dependent on a change of the reaction variable, as the thermodynamic ones, a linear rate–equilibrium relationship is found. A striking example in favor of this conclusion is the observation of Brønsted correlations with slopes outside the range 0–1, in the deprotonation of nitroalkane acids.[16]

In conclusion we share Arnett's strong skepticism about the meaning of the α parameter for anion–cation reactions in solutions in view of the great complexity of the potential surface, which must involve the motions of many solvent molecules.[17]

Relative Stability of 2*H* and 4*H* Adducts. 2*H*- and 4*H*-pyrans are fundamental heterocyclic systems;[18] however, to date, there are not quantitative data on their relative thermodynamic stability.

The ratio K_2/K_4, equivalent to the equilibrium constant for the isomerization of the 4*H*-pyran into the 2*H* one, is

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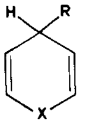
only slightly affected by the substituents on the phenyl ring ($K_2/K_4 \sim 2 \pm 1 \times 10^4$) in spite of the large range of variation of the individual equilibrium constants. This can be nicely shown by the excellent linear correlation of nearly unity slope between log K_4 and log K_2 spanning about seven powers of ten (plot not shown; slope = 1.06; r = 0.998). A similar behavior has been shown for the thiopyrylium series with $K_2/K_4 \sim 200$.[1] These data allow the evaluation of the standard free energy difference change between 2H and 4H adducts on changing sulfur with oxygen. This quantity calculated by the following equation:

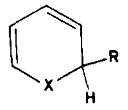
$$\Delta\Delta G^{\ominus} = -RT \ln\left[\left(\frac{K_2}{K_4}\right)_{\mathrm{O}} \Big/ \left(\frac{K_2}{K_4}\right)_{\mathrm{S}}\right] \qquad (8)$$

amounts to −2.7 ± 0.2 kcal/mol.

Because of cancellation of ring substituent[19] and solvent effects[20] in the ratio within square brackets, the $\Delta\Delta G^{\ominus}$ value can be used to predict the $\Delta G^{\ominus}$ for the isomerization of a given pyran if the $\Delta G^{\ominus}$ value for the isomerization of the corresponding thiopyran is known and vice versa. As a useful application we are going to estimate the relative thermodynamic stability of the unsubstituted 4H-pyran (**15**) and 2H-pyran (**16**). This determination would not be experimental feasible because **16** is a reactive intermediate undergoing a fast ring opening reaction to *cis*-2,4-pentadienal.[21]



15, X:O, R:H
17, X:S, R:OMe
19, X:S, R:H



16, X:O, R:H
18, X:S, R:OMe
20, X:S, R:H

Degani et al. isolated 2-methoxy-2H-thiopyran (**18**) as the only product of the reaction of unsubstituted thiopyrylium ion with a methanolic solution of $NaHCO_3$.[22] Since the methoxide attachment in methanol to thiopyrylium ions is a reversible process,[1,3b,c] the isolation of only the 2H adduct indicates that **18** is at least 50 times more stable than the 4H isomer **17**, i.e., $K_2/K_4 \geq 50$, corresponding to $\Delta G^{\ominus}(\mathbf{17} \rightarrow \mathbf{18}) \leq -2.3$ kcal/mol. Now we can safely assume that $\Delta G^{\ominus}(\mathbf{19} \rightarrow \mathbf{20}) \lesssim \Delta G(\mathbf{17} \rightarrow \mathbf{18}) \leq -2.3$ kcal/mol, where **19** and **20** refer to the unsubstituted 4H- and 2H-thiopyrans, respectively. This assumption is justified by data referring to 2,4,6-triphenylthiopyrans for which the rearrangements of methoxide and hydride ions can be compared. From the equilibrium constant for the isomerization of 4-methoxy-2,4,6-triphenyl-4H-thiopyran into the 2H isomer in MeOH at 25 °C (= 65),[19] we obtain a $\Delta G^{\ominus}$ value of −2.5 kcal/mol. Since 4H-2,4,6-triphenylthiopyran completely rearranges to the corresponding 2H isomer in boiling MeCN or AcOH,[23] we conclude that for this isomerization $\Delta G^{\ominus} \leq -2.3$ kcal/mol. Therefore, the hydride rearrangement from the γ to α position is as favored, at least, as the corresponding methoxide rearrangement.

Taking into account the $\Delta\Delta G^{\ominus}$ value for the sulfur-oxygen substitution we can estimate $\Delta G^{\ominus}(\mathbf{15} \rightarrow \mathbf{16})$, according to the following equation:

$$\Delta G^{\ominus}(\mathbf{15} \rightarrow \mathbf{16}) \simeq \Delta G^{\ominus}(\mathbf{19} \rightarrow \mathbf{20}) + \Delta\Delta G^{\ominus} \qquad (9)$$

Since $\Delta G^{\ominus}(\mathbf{19} \rightarrow \mathbf{20})$ is ≤ −2.3 kcal/mol and $\Delta\Delta G^{\ominus} = -2.7$ kcal/mol, we obtained $\Delta G^{\ominus}(\mathbf{15} \rightarrow \mathbf{16}) \leq -5.0$ kcal/mol. If statistical factors are taken into consideration we obtain $\Delta G^{\ominus}(\mathbf{15} \rightarrow \mathbf{16}) \leq -4.6$ kcal/mol and $\Delta G^{\ominus}(\mathbf{19} \rightarrow \mathbf{20}) \leq -1.9$ kcal/mol. This result shows that 2H-pyran (**16**) is at least 4.6 kcal/mol more stable than the 4H isomer **15**, thus disproving semiempirical and nonempirical quantum mechanical calculations that have indicated the reverse order of stability.[24]

It is interesting to compare the limit values of $\Delta G^{\ominus}(\mathbf{15} \rightarrow \mathbf{16})$ and $\Delta G^{\ominus}(\mathbf{19} \rightarrow \mathbf{20})$ with the corresponding data referring to the isomerization of 1,4-cyclohexadiene into the 1,3 isomer ($\Delta G^{\ominus}$ = 0.06 ± 0.04 kcal/mol at 25 °C)[25,26] and of N-methyl-1,4-dihydropyridine into the 1,2 ($\Delta G^{\ominus}$ = 2.29 ± 0.01 kcal/mol at 91.6 °C).[25,27]

From the $\Delta G^{\ominus}$ value obtained for the isomerization of cyclohexadienes it has been concluded that the 1,3-cyclohexadiene is devoid of conjugation.[26] The above data indicate that the substitution of a methylene group in 1,4- and 1,3-cyclohexadiene with a heteroatom (NMe, O, S) involves an energy differentiation between the two isomers whose direction is not easily foreseeable, with $\Delta G^{\ominus}$ being positive with NMe and negative with O and S.

Experimental Section

Materials. Methanol-d_4 for NMR spectroscopy was from Merck. Dry methanol was obtained as previously reported.[28] Stock solutions of sodium methoxide were prepared by dissolving the appropriate amount of clean sodium in methanol (or methanol-d_4) under an argon atmosphere. Methanolic $HClO_4$ was prepared by a published procedure.[29] Purification of triethylamine and preparation of triethylamine/triethylammonium buffers were carried out as previously indicated.[28] Chloroacetic acid (Aldrich Gold Label) was used without further purification. Chloroacetic acid/chloroacetate buffers were prepared by partial neutralization of the acid with sodium methoxide solutions.

2,6-Di-*tert*-butyl-4-(*p*-nitrophenyl)pyrylium trifluoromethanesulfonate (**1a**),[30] 2,6-di-*tert*-butyl-4-(*m*-chlorophenyl)pyrylium perchlorate (**2a**),[1] 2,6-di-*tert*-butyl-4-(*p*-chlorophenyl)pyrylium perchlorate (**3a**),[30] 2,6-di-*tert*-butyl-4-(*p*-methylphenyl)pyrylium perchlorate (**5a**),[30] 2,6-di-*tert*-butyl-4-(*p*-methoxyphenyl)pyrylium perchlorate (**6a**),[30] and 2,6-di-*tert*-butyl-4-(*p*-(dimethylamino)phenyl)pyrylium fluoroborate (**7a**)[30] were available from our previous work. 2,6-Di-*tert*-butyl-4-phenylpyrylium trifluoromethanesulfonate (**4a**) was prepared according to a literature procedure.[31]

^{1}H NMR Measurements. All spectra were recorded on a Bruker WP 80 SY spectrometer. Chemical shifts were quoted in ppm relative to Me_4Si. Low-temperature NMR spectra were

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[19] The K_2/K_4 values for the reaction of 2,4,6-triphenylpyrylium (= 4.15 × 10^3) and 2,4,6-triphenylthiopyrylium (= 65) cations with methoxide ion in methanol at 25 °C afford $\Delta\Delta G°$ = −2.5 kcal/mol, thus supporting the above statement (K_4 values are from ref 3b and K_2 values are data to be published).

[20] $[(K_2/K_4)_{\mathrm{O}}/(K_2/K_4)_{\mathrm{S}}]$ is solvent-independent because even the simple K_2/K_4 ratio is not affected by the change of solvent. In fact, methoxide attachment to 2,4,6-tri-*tert*-butylthiopyrylium ion carried out at 25 °C both in MeOH[3c] and in CH_3CN (unpublished results) afforded the same equilibrium mixture of 2H and 4H adducts.

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recorded just after the addition of the substrate (ca. 0.05 mmol of solid sample) to ca. 0.5 mL of a solution of CD_3ONa (0.5 M) in CD_3OD, thermostated at -30 °C inside the NMR probe. Room temperature (30 °C) NMR measurements were carried out after equilibrium of the reaction mixtures was attained. ^1H NMR data for cations **1a**–**7a**, 4*H*-pyrans **1b**–**6b**, and 2*H*-pyrans **1c**–**7c** follow.[32]

1a: δ 1.63 (s, 18 H, *t*-Bu), 8.46 (pseudo singlet, 4 H, H-2′, H-3′), 8.48 (s, 2 H, H-3).

2a: δ 1.60 (s, 18 H, *t*-Bu), 7.5–8.3 (m, 4 H, aryl), 8.32 (s, 2 H, H-3).

3a: δ 1.60 (s, 18 H, *t*-Bu), 7.73 (A_2B_2 system, 2 H, J = 9.0 Hz, H-3′), 8.23 (A_2B_2 system, 2 H, J = 9.0 Hz, H-2′), 8.31 (s, 2 H, H-3).

4a: δ 1.61 (s, 18 H, *t*-Bu), 7.7–8.3 (m, 5 H, phenyl), 8.35 (s, 2 H, H-3).

5a: δ 1.59 (s, 18 H, *t*-Bu), 2.51 (s, 3 H, Me), 7.54 (A_2B_2 system, 2 H, J = 8.6 Hz, H-3′), 8.19 (A_2B_2 system, 2 H, J = 8.6 Hz, H-2′), 8.27 (s, 2 H, H-3).

6a: δ 1.58 (s, 18 H, *t*-Bu), 3.98 (s, 3 H, OMe), 7.26 (A_2B_2 system, 2 H, J = 9.1 Hz, H-3′), 8.18 (s, 2 H, H-3), 8.35 (A_2B_2 system, 2 H, J = 9.1 Hz, H-2′).

7a: δ 1.50 (s, 18 H, *t*-Bu), 3.27 (s, 6 H, NMe_2), 6.99 (A_2B_2 system, 2 H, J = 9.4 Hz, H-3′), 7.81 (s, 2 H, H-3), 8.24 (A_2B_2 system, 2 H, J = 9.4 Hz, H-2′).

1b: δ 1.23 (s, 18 H, *t*-Bu), 4.63 (s, 2 H, H-3), 7.60 (A_2B_2 system, 2 H, J = 9.0 Hz, H-2′), 8.22 (A_2B_2 system, 2 H, J = 9.0 Hz, H-3′).

2b: δ 1.23 (s, 18 H, *t*-Bu), 4.60 (s, 2 H, H-3), 7.2–7.5 (m, 4 H, aryl).

3b: δ 1.22 (s, 18 H, *t*-Bu), 4.60 (s, 2 H, H-3), 7.34 (pseudo-singlet, 4 H, aryl).

4b: δ 1.21 (s, 18 H, *t*-Bu), 4.60 (s, 2 H, H-3), 7.31 (br s, 5 H, phenyl).

5b:[33] δ 1.22 (s, 18 H, *t*-Bu), 2.31 (s, 3 H, Me), 4.60 (s, 2 H, H-3).

6b: δ 1.21 (s, 18 H, *t*-Bu), 3.76 (s, 3 H, OMe), 4.62 (s, 2 H, H-3), 6.86 (A_2B_2 system, 2 H, J = 8.8 Hz, H-3′), 7.26 (A_2B_2 system, 2 H, J = 8.8 Hz, H-2′).

1c: δ 1.00 (s, 9 H, *t*-Bu-2), 1.23 (s, 9 H, *t*-Bu-6), 5.48 (d, 1 H, J = 1.6 Hz, H-3), 5.58 (d, 1 H, J = 1.6 Hz, H-5), 7.75 (A_2B_2 system, 2 H, J = 9.0 Hz, H-2′), 8.28 (A_2B_2 system, 2 H, J = 9.0 Hz, H-3′).

2c: δ 1.00 (s, 9 H, *t*-Bu-2), 1.23 (s, 9 H, *t*-Bu-6), 5.38 (pseudo-singlet, 2 H, H-3, H-5), 7.3–7.5 (m, 4 H, aryl).

3c: δ 1.01 (s, 9 H, *t*-Bu-2), 1.23 (s, 9 H, *t*-Bu-6), 5.40 (pseudo-singlet, 2 H, H-3, H-5), 7.38 (A_2B_2 system, 2 H, J = 9.0 Hz, H-2′), 7.47 (A_2B_2 system, 2 H, J = 9.0 Hz, H-3′).

4c: δ 1.01 (s, 9 H, *t*-Bu-2), 1.23 (s, 9 H, *t*-Bu-6), 5.38 (d, 1 H, J = 1.5 Hz, H-3), 5.40 (d, 1 H, J = 1.5 Hz, H-5), 7.5 (br s, 5 H, phenyl).

5c: δ 0.99 (s, 9 H, *t*-Bu-2), 1.21 (s, 9 H, *t*-Bu-6), 2.33 (s, 3 H, Me), 5.31 (d, 1 H, J = 1.4 Hz, H-3), 5.39 (d, 1 H, J = 1.4 Hz, H-5), 7.20 (A_2B_2 system, 2 H, J = 8.4 Hz, H-3′), 7.35 (A_2B_2 system, 2 H, J = 8.4 Hz, H-2′).

6c: δ 1.00 (s, 9 H, *t*-Bu-2), 1.23 (s, 9 H, *t*-Bu-6), 3.81 (s, 3 H, OMe), 5.31 (d, 1 H, J = 1.3 Hz, H-3), 5.41 (d, 1 H, J = 1.3 Hz, H-5), 6.97 (A_2B_2 system, 2 H, J = 8.8 Hz, H-3′), 7.46 (A_2B_2 system, 2 H, J = 8.8 Hz, H-2′).

7c: δ 1.00 (s, 9 H, *t*-Bu-2), 1.23 (s, 9 H, *t*-Bu-6), 2.95 (s, 6 H, NMe_2), 5.27 (d, 1 H, J = 1.5 Hz, H-3), 5.42 (d, 1 H, J = 1.5 Hz, H-5), 6.78 (A_2B_2 system, 2 H, J = 9.0 Hz, H-3′), 7.36 (A_2B_2 system, 2 H, J = 9.0 Hz, H-2′).

UV–Vis Spectra. The UV–vis spectra of the substrates and the corresponding 2*H* adducts in methanol were recorded on a Cary 219 spectrophotometer. The values of λ_{max} (log ϵ) follow.

1a, 310 nm (4.48); **2a**, 309 nm (4.38); **3a**, 342 nm (4.44), 307 nm (4.24); **4a**, 332 nm (4.31), 306 nm (4.24); **5a**, 353 nm (4.49), 304 nm (4.17); **6a**, 390 nm (4.62), 299 nm (4.12); **7a**, 499 nm (4.83), 288 nm (4.12).

1c, 346 nm (3.49), 283 nm (4.19); **2c**, 292 nm (3.49), 238 nm (4.31); **3c**, 292 nm (3.55), 245 nm (4.46); **4c**, 292 nm (3.59), 235 nm (4.35); **5c**, 288 nm (3.62), 242 nm (4.37); **6c**, 248 nm (4.37); **7c**, 290 nm (4.28).

Rate Measurements. Kinetic experiments were carried out on a Durrum 110 stopped-flow spectrophotometer at 25.0 °C under pseudo-first-order conditions with MeONa and/or Et_3N/Et_3NH^+ buffers. The ionic strength was always below 6×10^{-3} M. The methoxide ion concentration of each buffer was calculated from the pK_a value of Et_3N (10.88)[29] and from the methanol autoprotolysis constant (pK_{MeOH} = 16.92 at 25 °C)[34] according to the equation

$$[MeO^-] = \frac{K_{MeOH}}{K_a} \times \frac{[base]}{[acid]}$$

The reaction of cation **1a** was monitored at 320 nm. The reactions of the other cations were monitored at two wavelengths (λ_A and λ_B). The values of λ_A and λ_B (nm), in that order, are the following: **2a**, 360, 300; **3a**, 350, 300; **4a**, 340, 300; **5a**, 360, 300; **6a**, 410, 300; **7a**, 470, 300. The k_2/k_4 ratio for cations **2a**–**6a** was determined from absorbance measurements carried out at λ_B, at the end of the first and the second process, according to a previously described method.[1]

Equilibrium Measurements. The determination of K_2 values was carried out at 25.0 °C on a Cary 219 spectrophotometer, by measuring the residual absorbance of the substrate (OD_∞) after equilibrium with buffer solutions. The measurements were carried out at λ_A for the cations **2a**–**7a** (vide supra) and at λ = 320 nm for the cation **1a**. The addition of an excess of methanolic $HClO_4$ to these mixtures shifts the equilibrium completely toward the substrate, thus permitting the measurements of OD_0, after correction of the observed OD value for dilution.

The K_2 values were obtained by the equation

$$K_2 = \frac{(OD_0 - OD_\infty)}{OD_\infty \times [MeO^-]}$$

In the case of the cation **1a**, owing to the absorbance contribution of the 2*H* adduct **1c**, the observed OD_∞ value (OD_∞^{obs}) must be corrected by the equation

$$OD_\infty = \frac{OD_\infty^{obs}\epsilon_{1a} - OD_0\epsilon_{1c}}{\epsilon_{1a} - \epsilon_{1c}}$$

where ϵ_{1a} and ϵ_{1c} are the molar absorbances for **1a** and **1c** at λ = 320 nm, respectively. The buffers used were triethylamine/triethylammonium for the cation **7a** and chloroacetic acid/chloroacetate (pK_a = 7.7)[35] for the cations **1a**–**6a**. The methoxide ion concentration of each buffer was calculated from the methanol autoprotolysis constant (vide supra). The ionic strength was always lower than 3×10^{-3} M. The concentration of the substrates was in the range $1–4 \times 10^{-5}$ M. The absorbance measurements were carried out with Teflon-stoppered 1-cm quartz cells, with the exception of cation **1a** for which 10-cm quartz cells were used.

Acknowledgment. We thank Mr. G. Frachey for the technical assistance in NMR measurements.

Registry No. **1a**, 104241-41-0; **1b**, 104241-45-4; **1c**, 104241-50-1; **2a**, 104241-42-1; **2b**, 104241-46-5; **2c**, 104241-51-2; **3a**, 104241-43-2; **3b**, 104241-47-6; **3c**, 104241-52-3; **4a**, 75882-53-0; **4b**, 104086-44-4; **4c**, 81128-16-7; **5a**, 104241-44-3; **5b**, 104241-48-7; **5c**, 104241-53-4; **6a**, 62497-13-6; **6b**, 104241-49-8; **6c**, 104241-54-5; **7a**, 54827-40-6; **7c**, 104241-55-6.

Supplementary Material Available: Tables S1–S9 summarizing all the kinetic measurements (9 pages). Ordering information is given on any current masthead page.

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[32] In view of the use of deuteriated methanol, the chemical shift values of the 2- and 4-methoxy groups in the 2*H* and 4*H* adducts, respectively, are not quoted.

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