^{1}H Nuclear Magnetic Resonance Study of Methoxide Addition to Pyrylium and Thiopyrylium Cations; Heteroatom and Substituent Effects

Giancarlo Doddi * and Gianfranco Ercolani *
Centro C.N.R. di Studio sui Meccanismi di Reazione, c/o Dipartimento di Chimica, Università di Roma La Sapienza,' Piazzale Aldo Moro 2, I-00185 Roma

Methoxide addition to pyrylium and thiopyrylium salts with various α-substituents (Ph or Bu^t) and γ-substituents (H, Me, Bu^t, Et$_3$C, Ph, or MeO) in methanol at −40 and 25 °C has been studied by ^{1}H n.m.r. The composition of the product mixtures, kinetically controlled at −40 °C and thermodynamically controlled at 25 °C, gives information on the factors affecting positional selectivity and the relative thermodynamic stability of the addition products (the 2*H*- and 4*H*-adduct). The methyl-substituted substrates also undergo deprotonation, to yield the corresponding anhydro-bases. Analysis of heteroatom and substituent effects on the reaction course emphasizes the role of polar and steric interactions, and sheds light on the structures of the transition states.

The ambident cations pyrylium[1] and thiopyrylium[2] are particularly suitable for further elucidation of nucleophile–cation interactions.[3]

Here we report a ^{1}H n.m.r. study of the reactions of the cations (**1a**)—(**17a**) with methoxide ion in methanol at −40 and 25 °C. Our aim was to gain an understanding of the factors affecting nucleophilic addition by examining the role of the α- and γ-substituents and of the heteroatom on positional selectivity and the relative thermodynamic stability of the corresponding addition products (the 2*H*- and 4*H*-adducts).

Results

The reactions of the substrates (**1a**)—(**4a**), (**6a**)—(**8a**), and (**10a**)—(**17a**) with an excess of CD_3O^- in [$^2H_4$]methanol at −40 and 25 °C was studied by ^{1}H n.m.r.†

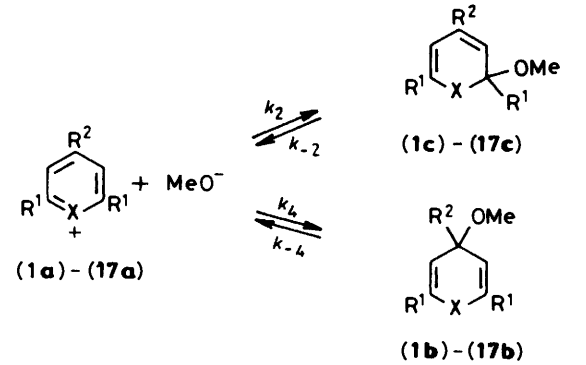
In general the reaction proceeds as shown in the Scheme. Some peculiarities are shown by the methyl-substituted cations (**6a**), (**11a**), and (**15a**), which also yield the corresponding anhydro-bases (**6d**), (**11d**), (**15d**); and by the cation (**5a**), which yields as final product the acyclic 5-methoxy-1,5-diphenylpenta-2,4-dienone.[4]

In Table 1 are reported the ^{1}H n.m.r. data of the substrates (**1a**)—(**17a**) in methanol. The cations (**6a**), (**11a**), and (**15a**) undergo hydrogen isotopic exchange with the solvent at the γ-methyl group. With the thiopyrylium derivatives (**11a**) and (**15a**) the process is slow enough to allow measurement of δ(CH_3) in CD_3OD.

In Table 2 are reported the ^{1}H n.m.r. data of the reaction products. The assignment of the chemical shift values is based on the multiplicity of the signals and on comparison with data reported for cognate reactions.[4,5] In view of the use of deuteriated methanol, the chemical shift values of the methoxy groups are not quoted. However, the ^{1}H n.m.r. spectra of the adducts isolated from CH_3OH solution and recorded in CCl_4 (not reported) indicate that the methoxy group is bound to an sp^3 carbon atom (δ 3.01—3.25).[6]

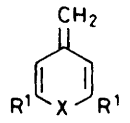
The chemical shift values of the 4-methyl groups of the 4*H*-adducts (**6b**), (**11b**), and (**15b**) and of the 2*H*-adduct (**6c**) were obtained by adding the corresponding substrates as solid samples to the methoxide solution. This procedure prevents H/D exchange at the methyl group, which is slower than adduct formation. Although the kinetics of the reactions of the cations (**5a**), (**8a**), (**9a**), and (**16a**) with MeO^- had been studied previously[7] (data in Table 4), they were included in this study to test the consistency of our analysis of the ^{1}H n.m.r. data.

† Methoxide addition to (**5a**) and (**9a**) had already been studied by n.m.r. both at low and at room temperature.[4]



	X	R^1	R^2		X	R^1	R^2
(1)	O	Bu^t	H	(10)	S	Bu^t	H
(2)	O	Bu^t	Bu^t	(11)	S	Bu^t	Me
(3)	O	Bu^t	Et$_3$C	(12)	S	Bu^t	Bu^t
(4)	O	Bu^t	Ph	(13)	S	Bu^t	Ph
(5)	O	Ph	H	(14)	S	Ph	H
(6)	O	Ph	Me	(15)	S	Ph	Me
(7)	O	Ph	Bu^t	(16)	S	Ph	Ph
(8)	O	Ph	Ph	(17)	S	Ph	OMe
(9)	O	Ph	OMe				

Scheme.



(**6d**) X = O, R^1 = Ph
(**11d**) X = S, R^1 = Bu^t
(**15d**) X = S, R^1 = Ph

Low-temperature N.m.r. Experiments.—At −40 °C the reactions of the cations (**1a**)—(**17a**) with an excess of CD_3O^-

Table 1. ^{1}H N.m.r. data for pyrylium and thiopyrylium cations in CD_3OD (δ values)

Compound	
(1a)	1.56 (18 H, s, 2- and 6-Bu^t), 8.27 (2 H, m, *J* 8.8 Hz, 3- and 5-H), 9.10 (1 H, m, *J* 8.8 Hz, 4-H).
(2a)	1.47 (9 H, s, 4-Bu^t), 1.54 (18 H, s, 2- and 6-Bu^t), 8.00 (2 H, s, 3- and 5-H).
(3a)	0.77 (9 H, t, *J* 7.0 Hz, CH_3CH_2), 1.53 (18 H, s, 2- and 6-Bu^t), 1.90 (6 H, q, *J* 7.0 Hz, CH_3CH_2), 7.87 (2 H, s, 3- and 5-H).
(4a)	1.61 (18 H, s, 2- and 6-Bu^t), 7.7—8.3 (5 H, m, 4-Ph), 8.35 (2 H, s, 3-and 5-H).
(5a)	7.7—8.5 (10 H, m, 2- and 6-Ph), 8.71 (2 H, m, *J* 8.4 Hz, 3- and 5-H), 9.04 (1 H, m, *J* 8.4 Hz, 4-H).
(6a)[a]	7.7—8.5 (10 H, m, 2- and 6-Ph), 8.64 (2 H, s, 3- and 5-H).
(7a)	1.60 (9 H, s, 4-Bu^t), 7.7—8.5 (10 H, m, 2- and 6-Ph), 8.62 (2 H, s, 3- and 5-H).
(8a)	7.7—8.6 (15 H, m, 2-, 4-, and 6-Ph), 8.98 (2 H, s, 3- and 5-H).
(9a)[b]	4.43 (3 H, s, OCH_3), 7.8—8.4 (10 H, m, 2- and 6-Ph), 8.06 (2 H, s, 3- and 5-H).
(10a)	1.65 (18 H, s, 2- and 6-Bu^t), 8.86 (3 H, pseudo-singlet, 3-, 4-, and 5-H).
(11a)	1.63 (18 H, s, 2- and 6-Bu^t), 2.88 (3 H, s, 4-Me), 8.76 (2 H, s, 3- and 5-H).
(12a)	1.57 (9 H, s, 4-Bu^t), 1.67 (18 H, s, 2- and 6-Bu^t), 8.73 (2 H, s, 3- and 5-H).
(13a)	1.70 (18 H, s, 2- and 6-Bu^t), 7.7—8.2 (5 H, m, 4-Ph), 8.82 (2 H, s, 3- and 5-H).
(14a)	7.7—8.2 (10 H, m, 2- and 6-Ph), 9.01 (3 H, pseudo-singlet, 3-, 4-, and 5-H).
(15a)	3.00 (3 H, s, 4-Me), 7.7—8.2 (10 H, m, 2- and 6-Ph), 8.91 (2 H, s, 3- and 5-H).
(16a)[c]	7.6—8.4 (15 H, m, 2-, 4-, and 6-Ph), 9.20 (2 H, s, 3- and 5-H).
(17a)	4.50 (3 H, s, 4-OCH_3), 7.7—8.3 (10 H, m, 2- and 6-Ph), 8.43 (2 H, s, 3- and 5-H).

[a] Determination of the 4-Me chemical shift is prevented by fast H–D exchange with the solvent. [b] Spectrum recorded at 55 °C in CH_3OD. [c] Ref. 5*a*.

Table 2. ^{1}H N.m.r. data for 4*H*- and 2*H*-adducts and anhydro-bases in CD_3OD (δ values)

Compound	
(1b)	1.18 (18 H, s, 2- and 6-Bu^t), 4.65 (1 H, t, *J* 4.2 Hz, 4-H), 4.91 (2 H, d, *J* 4.2 Hz, 3- and 5-H).
(2b)	0.84 (9 H, s, 4-Bu^t), 1.17 (18 H, s, 2- and 6-Bu^t), 4.59 (2 H, s, 3- and 5-H).
(3b)[a]	1.17 (18 H, s, 2- and 6-Bu^t), 4.57 (2 H, s, 3- and 5-H).
(4b)	1.21 (18 H, s, 2- and 6-Bu^t), 4.60 (2 H, s, 3- and 5-H), 7.31 (5 H, br s, 4-Ph).
(5b)[b]	4.90 (1 H, t, *J* 4.5 Hz, 4-H), 5.85 (2 H, d, *J* 4.5 Hz, 3- and 5-H), 7.1—8.1 (10 H, m, 2- and 6-Ph).
(6b)	1.54 (3 H, s, 4-Me), 5.60 (2 H, s, 3- and 5-H), 7.2—8.0 (10 H, m, 2- and 6-Ph).
(7b)	Not observed
(8b)	Hidden signals (see text)
(9b)[b]	5.80 (2 H, s, 3- and 5-H), 7.3—8.1 (10 H, m, 2- and 6-Ph).
(10b)	1.23 (18 H, s, 2- and 6-Bu^t), 4.80 (1 H, t, *J* 5.6 Hz, 4-H), 5.74 (2 H, d, *J* 5.6 Hz, 3- and 5-H).
(11b)	1.25 (18 H, s, 2- and 6-Bu^t), 1.33 (3 H, s, 4-Me), 5.38 (2 H, s, 3- and 5-H).
(12b)	0.84 (9 H, s, 4-Bu^t), 1.25 (18 H, s, 2- and 6-Bu^t), 5.47 (2 H, s, 3- and 5-H).
(13b)	1.26 (18 H, s, 2- and 6-Bu^t), 5.39 (2 H, s, 3- and 5-H), 7.32 (5 H, br s, 4-Ph).
(14b)	5.18 (1 H, t, *J* 5.2 Hz, 4-H), 6.23 (2 H, d, *J* 5.2 Hz, 3- and 5-H), 7.4—7.7 (10 H, m, 2- and 6-Ph).
(15b)	1.49 (3 H, s, 4-Me), 5.90 (2 H, s, 3- and 5-H), 7.2—7.7 (10 H, m, 2- and 6-Ph).
(16b)	5.91 (2 H, s, 3- and 5-H), 7.2—7.7 (15 H, m, 2-, 4-, and 6-Ph).
(17b)	6.05 (2 H, s, 3- and 5-H), 7.3—7.8 (10 H, m, 2- and 6-Ph).
(1c)	0.97 (9 H, s, 2-Bu^t), 1.16 (9 H, s, 6-Bu^t), 5.06 (1 H, m, *J* 6 and 0.7 Hz, 3-H), 5.15 (1 H, m, *J* 10 and 0.7 Hz, 5-H), 6.31 (1 H, m, *J* 10 and 6 Hz, 4-H).
(2c)	0.93 (9 H, s, 2-Bu^t), 1.11 (9 H, s, 4-Bu^t), 1.17 (9 H, s, 6-Bu^t), 4.84 (1 H, d, *J* 1.5 Hz, 3-H), 5.10 (1 H, d, *J* 1.5 Hz, 5-H).
(3c)	0.71 (9 H, t, *J* 7.2 Hz, CH_3CH_2), 0.95 (9 H, s, 2-Bu^t), 1.17 (9 H, s, 6-Bu^t), 1.45 (6 H, q, *J* 7.2 Hz, CH_3CH_2), 4.84 (1 H, d, *J* 1.0 Hz, 3-H), 5.05 (1 H, d, *J* 1.0 Hz, 5-H).
(4c)[c]	1.01 (9 H, s, 2-Bu^t), 1.23 (9 H, s, 6-Bu^t), 5.38 (1 H, d, *J* 1.5 Hz, 3-H), 5.40 (1 H, d, *J* 1.5 Hz, 5-H), 7.5 (5 H, br s, 4-Ph).
(5c)	Not observed
(6c)	1.95 (3 H, d, *J* 1.5 Hz, 4-Me), 5.21 (1 H, m, *J* 1.5 and 1.5 Hz, 3-H), 6.16 (1 H, d, *J* 1.5 Hz, 5-H), 7.2—8.0 (10 H, m, 2- and 6-Ph).
(7c)	1.19 (9 H, s, 4-Bu^t), 5.22 (1 H, d, *J* 1.5 Hz, 3-H), 6.27 (1 H, d, *J* 1.5 Hz, 5-H), 7.4—7.8 (10 H, m, 2- and 6-Ph).
(8c)[d]	5.63 (1 H, d, *J* 1.4 Hz, 3-H), 6.50 (1 H, d, *J* 1.4 Hz, 5-H), 7.2—8.0 (15 H, m, 2-, 4-, and 6-Ph).
(9c)[b]	4.55 (1 H, d, *J* 2.0 Hz, 3-H), 6.00 (1 H, d, *J* 2.0 Hz, 5-H), 7.3—8.1 (10 H, m, 2- and 6-Ph).
(10c)	1.06 (9 H, s, 2-Bu^t), 1.26 (9 H, s, 6-Bu^t), 5.29 (1 H, d, *J* 10.2 Hz, 3-H), 6.00 (1 H, d, *J* 7.0 Hz, 5-H), 6.40 (1 H, m, *J* 10.2 and 7.0 Hz, 4-H).
(11c)	Not observed
(12c)	1.02 (9 H, s, 2-Bu^t), 1.16 (9 H, s, 4-Bu^t), 1.27 (9 H, s, 6-Bu^t), 5.16 (1 H, s, 3-H), 6.17 (1 H, s, 5-H).
(13c)	1.10 (9 H, s, 2-Bu^t), 1.33 (9 H, s, 6-Bu^t), 5.48 (1 H, s, 3-H), 6.33 (1 H, s, 5-H), 7.40 (5 H, br s, 4-Ph).
(14c)	5.47 (1 H, m, *J* 7.7 and 0.8 Hz, 3-H), 6.65 (1 H, m, *J* 7.7 and 6.0 Hz, 4-H), 6.75 (1 H, m, *J* 6.0 and 0.8 Hz, 5-H), 7.2—7.7 (10 H, m, 2- and 6-Ph).
(15c)	2.16 (3 H, d, *J* 1.0 Hz, 4-Me), 5.60 (1 H, q, *J* 1.0 Hz, 3-H), 6.60 (1 H, s, 5-H), 7.2—7.7 (10 H, m, 2- and 6-Ph).
(16c)[d]	5.66 (1 H, s, 3-H), 6.93 (1 H, s, 5-H), 7.3—7.8 (15 H, m, 2-, 4-, and 6-Ph).
(17c)	Not observed
(6d)	4.46 (2 H, s, 4-H_2), 6.41 (2 H, s, 3- and 5-H), 7.1—7.8 (10 H, m, 2- and 6-Ph).
(11d)	1.19 (18 H, s, 2- and 6-Bu^t), 4.48 (2 H, s, 4-H_2), 6.21 (2 H, s, 3- and 5-H).
(15d)	4.84 (2 H, s, 4-H_2), 6.72 (2 H, s, 3- and 5-H), 7.2—7.7 (10 H, m, 2- and 6-Ph).

[a] The ethyl group signals are hidden by the corresponding signals of the 2*H*-adduct (3c). [b] Ref. 4. [c] The assignments of the 3-H and 5-H signals may be interchanged. [d] Ref 5*a*.

lead to the immediate disappearance of the signals of the substrate (Table 1) and the appearance at higher field (owing to neutralization of the positive charge) of the signals of the corresponding adducts (Table 2); molar ratios (4*H*/2*H*) are reported in Table 3. At this temperature isomer equilibration is very slow and the composition of the reaction mixture is subject to kinetic control; therefore the isomer ratios reported in Table 3 coincide with the corresponding values of k_4/k_2 (Scheme). This behaviour is general, with the exception of the adducts from the cations (**4a**) and (**9a**), equilibration of which is not negligible even at this low temperature. In this case the 4*H*/2*H* ratio must be considered as a lower limit, *i.e.* $k_4/k_2 > 4H/2H$.

Owing to the presence of some non-deuteriated hydroxy groups, the signal of which appears close to where the β ring protons of the 4*H*-adduct (**8b**) were expected to absorb, we were not able to measure the corresponding 4*H*/2*H* ratio; in Table 3 we therefore report for the cation (**8a**) the corresponding kinetic ratio k_4/k_2 at 25 °C, obtained from the data reported in Table 4.

Table 3. Molar ratios (4*H*/2*H*) determined by ^{1}H n.m.r. at −40 and 25 °C [a]

Substrate	−40 °C	25 °C
(1a)	>50	<0.02
(2a)	0.44	<0.02
(3a)	0.11	<0.02
(4a)	2.7[b]	<0.02
(5a)	>50[c]	*d*
(6a)	1.1[b,d]	*d*
(7a)	<0.02	<0.02
(8a)	(0.11)[e]	<0.02
(9a)	2[b]	0.9
(10a)	>50	0.16
(11a)	>50	*d*
(12a)	1.7	0.12
(13a)	4.6	<0.02
(14a)	>50	0.94
(15a)	~30	*d*
(16a)	1.5	<0.02
(17a)	>50	>50

[a] The ratio 4*H*/2*H* is quoted as >50 or <0.02 when only one of the two adducts was detected [b] The reported value is lower than the k_4/k_2 ratio (see text). [c] Ref. 4. [d] Further details on the composition of the reaction mixture are reported in the text. [e] Estimated value (see text).

The assumption that k_4/k_2 does not change appreciably with temperature is justified by the observation that the 4*H*/2*H* ratio measured for the reaction of (**16a**) (1.5:1) is in excellent agreement with the k_4/k_2 ratio (1.4:1) obtained kinetically at 25 °C (Table 4).

As particular cases of the general Scheme, the cations (**1a**), (**5a**), (**10a**), (**11a**), (**14a**), and (**17a**) yield only the corresponding 4*H*-adducts (4*H*/2*H* > 50; Table 3), whereas the cation (**7a**) yields only the corresponding 2*H*-adduct (4*H*/2*H* < 0.02; Table 3).

The cation (**6a**) yields, together with the 4*H*- and 2*H*-pyran, also the corresponding anhydro-bases [molar ratios (**6b**):(**6c**):(**6d**) 1.1:1:0.24].

Room-temperature N.m.r. Experiments.—The ^{1}H n.m.r. spectra of the reaction mixtures were recorded at 25 °C after equilibrium was attained. The resulting thermodynamically controlled isomer ratios (Table 3) coincide with the corresponding ratios of the equilibrium constants, *i.e.* K_4/K_2. The experiments indicate that, with the exception of the reactions of (**7a**) and (**17a**), the compositions of the equilibrated reaction mixtures differ from those observed at low temperature.

Cations (**1a**)—(**4a**), (**8a**), (**13a**), and (**16a**) yielded only the corresponding 2*H*-adducts, whereas the cation (**5a**) yields as final product the acyclic 5-methoxy-1,5-diphenylpenta-2,4-dienone.[4] This compound is probably produced by fast ring-opening of the 2*H*-pyran (**5c**) (not detected in the reaction mixture).

The γ-methyl substituted cations (**6a**), (**11a**), and (**15a**)* were completely converted into the corresponding anhydro-bases.

Discussion

The data obtained at −40 and at 25 °C for the reactions of the cations (**1a**)—(**17a**) permit the first systematic comparison of the behaviour of pyrylium and thiopyrylium cations towards a nucleophilic reagent such as methoxide ion.

* Transient increments of the signals of the 2*H*-thiopyran (**15c**) were observed before equilibrium was attained. This indicates that the order of stability is (**15d**) > (**15c**) > (**15b**), whereas the rates of formation follow the inverse order.

Table 4. Rate and equilibrium constants for the reactions of the cation (**5a**), (**8a**), (**9a**), and (**16a**) with methoxide ion in MeOH at 25 °C

	k_4/l mol^{-1} s^{-1}	k_2[a]/l mol^{-1} s^{-1}	K_4/l mol^{-1}	K_2[a]/l mol^{-1}
(5a)[b]	1.1×10^8			
(8a)[c]	6.3×10^5	5.9×10^6	6.9×10^5	
(9a)[b]	$3.1_5 \times 10^6$	$5.0_5 \times 10^5$	$3.3_5 \times 10^6$	$3.6_5 \times 10^6$
(16a)[c]	1.8×10^5	1.3×10^5	2.6×10^6	

[a] Uncorrected for the statistical factor. [b] Ref. 7*a*. [c] Ref. 7*b*.

Substituent Effects.—The k_2 values for (**8a**) and (**9a**) (Table 4) differ by only a factor of 10 in spite of the great difference between the electronic effects of phenyl and methoxy; therefore we can confidently assume that when the γ-substituent is H, Me, Bu^t, Et$_3$C, or Ph, the k_2 values are even more similar to each other, provided that the heteroatom and the α-substituents are not changed. Comparisons between k_4/k_2 values will thus reflect essentially variation in the k_4 terms, *i.e.* $(k_4/k_2)_a/(k_4/k_2)_b \simeq (k_4)_a/(k_4)_b$. Thus the data reported in Table 3 indicate that k_4 decreases in the order H > Me > Ph > Bu^t > Et$_3$C.

The same order is observed in the base-catalysed hydrolysis of esters with substituents in the acyl component;[8]† this can be considered a model for our reaction since in both cases a nucleophilic addition on a trigonal carbon atom occurs. These facts suggest that the relative importance of polar and steric effects of the substituents is similar in the two reaction series.

With the thiopyrylium cations (and probably also with the pyrylium ones) the variation of the γ-substituent affects the relative stability of the two adduct (K_4/K_2) in the order: MeO > H ~ Bu^t > Ph. In this respect the effect of the methoxy group is spectacular, (**9a**) being the only pyrylium salt for which $K_4 \simeq K_2$ and (**17a**) the only thiopyrylium cation that does not give the 2*H*-adduct.

The K_4/K_2 values obtained with symmetrically substituted pyrylium and thiopyrylium cations indicate that 2*H*-adducts are intrinsically more stable than 4*H*-adducts. Higher stability of the neutral 2*H*-adducts[10] was observed also in methoxide addition to unsubstituted thiopyrylium cation‡ and in amine addition to 2,4,6-triphenylthiopyrylium cation (**16a**).[11] Moreover, Dimroth and his co-workers have reported the photochemical rearrangement of 4-benzyl-2,4,6-triphenyl-4*H*-pyran and -thiopyran to the corresponding 2*H*-adducts.[12] Since the 2*H*-adduct could revert to the 4*H*-isomer by a photochemical pathway (light of the frequency used would excite both adducts), the reaction course is governed by the relative stability of the two adducts. These data disprove quantum mechanical calculations carried out for unsubstituted 2*H*- and 4*H*-pyrans that indicate the reverse order of stability.[13]

It is interesting that in the majority of cases the 4*H*-adduct is the principal product of kinetic control whereas the 2*H*-adduct is the principal product of thermodynamic control, *i.e.* $k_4/k_2 > 1$ and $K_4/K_2 < 1$. Substituent effects play an important role in determining k_4/k_2 and K_4/K_2 values; nevertheless k_4/k_2 is always higher than K_4/K_2. These results suggest that the structural features responsible for the different stabilities of the two adducts are not present in the corresponding activated complexes, thus indicating that the transition states are ion pair-like.

† The experimental value for the base-catalysed hydrolysis of the ester with an Et$_3$C group is not reported. However, this value can be estimated from the corresponding E_s[9] and σ* values. The latter can be evaluated by applying the additivity rule to group polar effects.[9]

‡ In contrast, charged 2*H*- and 4*H*-adduct intermediates in amine addition to (**16a**) showed similar stabilities.[11]

The data reported in Table 3 indicate that the anhydro-bases generated from the methyl-substituted cations are always more stable than the corresponding 4*H*- and 2*H*-adducts. The higher stability of the anhydro-bases can be explained in terms of the aromatic character of their resonance structures involving charge separation. In spite of their greater stability the anhydro-bases are formed at a lower rate than the 4*H*- and 2*H*-adducts. This result is interesting because it indicates that proton transfer between positively charged carbon acids and the strong base MeO^- takes place well below the diffusion limit, as observed for neutral carbon acids.[14]

Heteroatom Effects.—The positional selectivity k_4/k_2 as measured by the ratio 4*H*/2*H* at −40 °C (Table 3) is always higher for thiopyrylium than for the corresponding pyrylium cations, in accord with non-empirical calculations[15] showing that the ratio of the positive charge densities between γ- and α-positions is higher for the thiopyrylium cation. These findings suggest that positional selectivity is affected by Coulombic interactions between the nucleophile and the reactive positions of the electrophile, supporting the view of ion pair-like transition states.

Significant differences between pyrylium and thiopyrylium cations are also shown in the relative thermodynamic stability, K_4/K_2, as measured by the 4*H*/2*H* ratios at 25 °C, K_4/K_2 being larger for the thiopyrylium than for the corresponding pyrylium derivatives. The K_4 values for the reaction of the pyrylium cation (**8a**) and the corresponding thiopyrylium ion (**16a**) (Table 4) are similar, thus indicating that the aforementioned trend is probably due to a decrease in the K_2 value on going from pyrylium to thiopyrylium.

As already observed for some methyl-substituted pyrylium and thiopyrylium cations,[16] the pyrylium ion (**6a**) in CD_3OD undergoes hydrogen isotopic exchange at the methyl group faster than the thiopyrylium cations (**11a**) and (**15a**). This behaviour has been explained in terms of the lower aromaticity of pyrylium with respect to thiopyrylium ions.[16]

It is interesting that only in the case of the cation (**5a**) did we observe a ring-opening reaction leading to 5-methoxy-1,5-diphenylpenta-2,4-dienone [the acyclic valence tautomer of the 2*H*-pyran (**5c**), not detected in the reaction mixture]. Katritzky *et al.* have pointed out that bulky ring substituents, preventing coplanarity of the conjugated system, destabilize the acyclic tautomer.[17] Our data confirm this statement since the product of ring opening of (**5c**) would be the less hindered one. In contrast with (**5c**), the corresponding thiopyran (**14c**) does not undergo such electrocyclic ring opening, in agreement with the well known behaviour of other 2*H*-thiopyrans.[5b,18]

Conclusions

From this study the following conclusions may be drawn: (i) positional selectivity of the addition of methoxide ion to pyrylium and thiopyrylium cations is affected by the charge density at the reaction centres (α- and γ-positions); (ii) although the transition states leading to the corresponding 4*H*- and 2*H*-adducts are ion pair-like, nevertheless the reaction is sensitive to steric hindrance by the substituents; (iii) 2*H*-adducts are intrinsically more stable than 4*H*-adducts but substituent effects in some cases can obscure this pattern; (iv) anhydro-bases are more stable than the corresponding 4*H*- and 2*H*-adducts but are formed at a lower rate.

Experimental

Materials.—[$^2H_4$]Methanol for n.m.r. spectroscopy was from Merck. Methoxide solutions were prepared by dissolving the appropriate amount of clean sodium in [$^2H_4$]methanol under argon. Published procedures were followed for the synthesis of 2,6-di-t-butylpyrylium perchlorate (**1a**),[19] 2,4,6-tri-t-butylpyrylium perchlorate (**2a**),[20] 2,6-di-t-butyl-4-phenylpyrylium trifluoromethanesulphonate (**4a**),[17] 2,6-diphenylpyrylium perchlorate (**5a**),[21] 2,6-diphenyl-4-methylpyrylium perchlorate (**6a**),[12] 2,4,6-triphenylpyrylium perchlorate (**8a**),[22] 2,6-diphenyl-4-methoxypyrylium perchlorate (**9a**),[23] 2,6-diphenyl-4-(methyl)thiopyrylium perchlorate (**15a**),[24] 2,4,6-triphenylthiopyrylium perchlorate (**16a**),[25] and 2,6-diphenyl-4-methoxythiopyrylium perchlorate (**17a**).[26]

2,6-Di-t-butylthiopyrylium perchlorate (**10a**),[27] 2,4,6-tri-t-butylthiopyrylium perchlorate (**12a**),[28] 2,6-di-t-butyl-4-(phenyl)thiopyrylium perchlorate (**13a**),[28] and 2,6-diphenylthiopyrylium perchlorate (**14a**)[27] were available from our previous work.

2,6-Di-t-butyl-4-(methyl)thiopyrylium tetrafluoroborate (**11a**) was prepared from (**10a**) according to a literature method.[29]

The preparation of 2,6-di-t-butyl-4-(1,1-diethylpropyl)-pyrylium perchlorate (**3a**) will be described elsewhere.

2,6-*Diphenyl-4-t-butylpyrylium perchlorate* (**7a**) was prepared by treating (**5a**) with Bu^{t}MgCl to yield the corresponding 4*H*-pyran; this was treated with anhydrous $FeCl_3$ in boiling acetic acid to give the corresponding pyrylium chloroferrate according to the procedure described by Dimroth *et al.* for 2,6-diphenyl-4-methylpyrylium chloroferrate.[12] Anion exchange was performed by dissolving the pyrylium chloroferrate in aqueous acetic acid (10% v/v) and then adding 70% $HClO_4$ in drops until precipitation of (**7a**) was complete (overall yield 28%); m.p. 195—197 °C (Found: C, 64.8; H, 5.4. $C_{21}H_{21}ClO_5$ requires C, 64.9; H, 5.4%).

^1H *N.m.r. Measurements.*—All spectra were recorded with a Bruker WP 80 SY spectrometer. Chemical shifts are quoted in p.p.m. relative to Me_4Si. The spectra of the substrates (**1a**)—(**17a**) (Table 1), recorded at room temperature, were of *ca.* 1—10 mg ml^{-1} samples, depending on solubility. Low-temperature spectra were recorded just after the addition of the substrate (*ca.* 10—20 μl of a *ca.* 1M CD_3OD solution, or *ca.* 0.05 mmol of solid) to *ca.* 0.5 ml of a 0.5M-solution of CD_3ONa in CD_3OD, thermostatted at −40 °C in the n.m.r. probe. The spectra at 25 °C were recorded after equilibration of the reaction mixtures.

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