Thiopyrylium Cations as Appropriate Compounds for the Quantitative Evaluation of *ipso*-Substituent Effects

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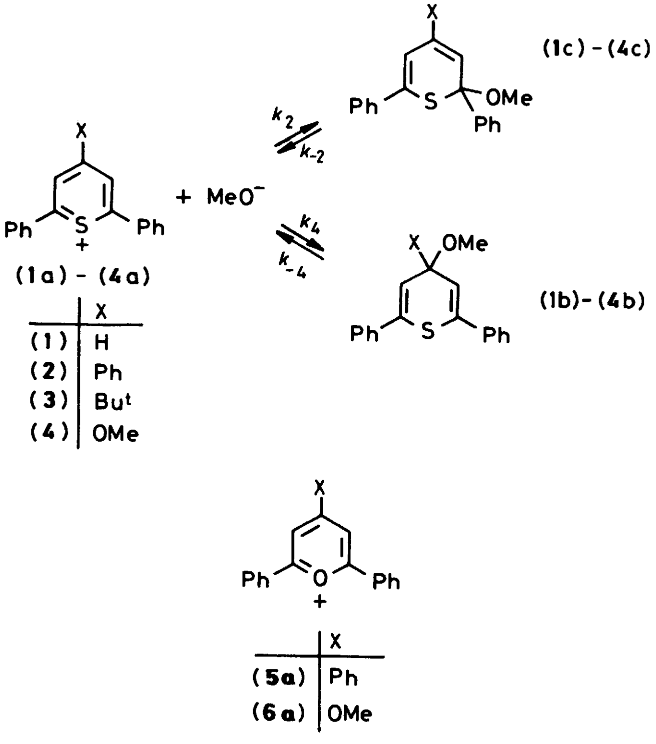
The kinetic and equilibrium constants for the reaction of 2,6-diphenyl-4-X-thiopyrylium cations (X = H, Ph, $\mathrm{Bu^t}$, or OMe) with methoxide ion to yield the corresponding 2*H*- and 4*H*-adducts have been determined in MeOH at 25 °C. The completion of an analogous study for 2,4,6-triphenylpyrylium ion is also reported. The equilibrium data allow the quantitative evaluation, in free energy terms, of *ipso*-effects relative to H (OMe, *ca.* −12; $\mathrm{Bu^t}$ *ca.* 0; Ph *ca.* 10 kJ $\mathrm{mol^{-1}}$). The estimate of the *gem*-dimethoxy stabilisation is in accordance with a previous estimate based on data referring to the formation of negatively charged Meisenheimer adducts. Although steric interactions between the geminal groups seem to be negligible in the final adducts, the kinetics data suggest that they occur in the transition states. This observation further supports our previous hypothesis of an ion-pair-like transition state for this class of reactions.

Pyrylium and thiopyrylium cations, at variance with neutral aromatic substrates, do not need the presence of electron-withdrawing substituents on the ring to undergo attack by nucleophiles. This peculiarity makes them ideal substrates to investigate the effects of *ipso*-substituents. Indeed with these cations measured effects are free from complicating steric factors due to activating groups flanking the *ipso*-substituent, as present in more classical substrates, such as 1-X-2,4,6-trinitrobenzenes.[1]

We report here a detailed kinetic and thermodynamic study of the reaction of 2,6-diphenyl-4-X-thiopyrylium cations (**1a**)—(**4a**) with methoxide ion in methanol at 25 °C, to evaluate the effect of Ph, $\mathrm{Bu^t}$, and OMe as *ipso*-substituents. We have already reported a partial kinetic study of the reaction of the cation (**2a**) and of its oxygenated analogue 2,4,6-triphenylpyrylium (**5a**).[2] Here we report data which complete the previous study. The reaction of the cation (**5a**) has been included because it is relevant to the present investigation.



Scheme 1.

Results

^{1}H *N.m.r. Study*.—Methoxide attachment to compounds (**1a**), (**2a**), and (**4a**) had already been studied by ^{1}H n.m.r. both at low (−40 °C) and at room (25 °C) temperature.[3] This study has been extended to the cation (**3a**) (see Experimental section). In general the reaction proceeds as shown in Scheme 1. At low temperature the reaction is under kinetic control; the cations (**1a**) and (**4a**) show only the formation of the 4*H*-thiopyrans (**1b**) and (**4b**), respectively, whereas the cations (**2a**) and (**3a**) show the formation of both adducts with molar ratios (4*H*:2*H*) 1.5:1 and 0.48:1, respectively. These isomer ratios, owing to the kinetic control, coincide with the corresponding k_4/k_2 values. We have evidence that k_4/k_2 does not change appreciably with temperature. Indeed kinetic investigations carried out at 25 °C for the cation (**2a**)[2] and for 2,6-di-t-butyl-4-phenylthiopyrylium[4] afforded k_4/k_2 values in excellent agreement with molar ratios (4*H*:2*H*) obtained by ^{1}H n.m.r. at low temperature.[3] Moreover in the case of the cations (**1a**) and (**3a**), since the equilibration process is sufficiently slow at 25 °C also, the same patterns as observed at −40 °C can be detected, if the spectra are recorded just after mixing of the reactants.

When the reaction mixtures are allowed to equilibrate at 25 °C, the cations (**1a**) and (**3a**) yield mixtures of adducts with molar ratios (4*H*:2*H*) 0.94:1 and 0.62_5:1, respectively. These isomer ratios coincide with the corresponding ratios of the equilibrium constants, *i.e.* K_4/K_2. The cations (**2a**) and (**4a**) yield exclusively the 2*H*-adduct (**2c**) and the 4*H*-adduct (**4b**), respectively. In this respect the behaviour of the cation (**4a**) is singular because the outcome is the same whether the reaction is carried out under conditions of kinetic or thermodynamic control.

Kinetic and Thermodynamic Studies.—The kinetic experiments were carried out in methanol at 25.0 °C, under pseudo-first-order conditions, by mixing the substrates with a large excess of sodium methoxide or $\mathrm{Et_3N{-}Et_3NH^+}$ buffer depending on the reactivity of the substrate (see Experimental section). In

Table 1. Rate and equilibrium constants for the reactions of the cations (**1a**)—(**6a**) with methoxide ion in MeOH at 25 °C

Cation	k_4 / mol^{-1} dm^3 s^{-1}	k_{-4} / s^{-1}	K_4 / mol^{-1} dm^3	k_2 [a] / mol^{-1} dm^3 s^{-1}	k_{-2} / s^{-1}	K_2 [a] / mol^{-1} dm^3
(**1a**)	$2.6_5 \times 10^{7}$	$2.6_5 \times 10^{-2}$	1.0×10^{9}	$2.9_5 \times 10^{5}$	2.8×10^{-4}	$1.0_5 \times 10^{9}$
(**2a**)	1.8×10^{5} [b]	7.0×10^{-2} [b]	2.6×10^{6} [b]	1.3×10^{5} [b]	$7.6_5 \times 10^{-4}$	1.7×10^{8}
(**3a**)	4.7×10^{4}	$1.2_5 \times 10^{-3}$	3.8×10^{7}	9.9×10^{4}	1.6×10^{-3}	6.1×10^{7}
(**4a**)	3.2×10^{6}	5.3×10^{-1} [a]	6.0×10^{6} [a]			*ca.* 8×10^{4} [c]
(**5a**)	6.3×10^{5} [b]	6.7×10^{-1} [b]	9.4×10^{5} [b]	5.9×10^{6} [b]	1.5×10^{-3}	3.9×10^{9}
(**6a**)	$3.1_5 \times 10^{6}$ [d]	9.4×10^{-1} [a,d]	$3.3_5 \times 10^{6}$ [a,d]	$5.0_5 \times 10^{5}$ [d]	1.4×10^{-1} [d]	$3.6_5 \times 10^{6}$ [d]

[a] Uncorrected for the statistical factor. [b] Ref. 2. [c] Estimated value (see Discussion section). [d] Ref. 10.

the kinetic experiments carried out with Et_3N–Et_3NH^+ buffer we had no evidence of general acid–base buffer catalysis. The kinetic study of the reaction of the cation (**2a**) has been reported previously.[2] The reactions of the cations (**1a**) and (**3a**) showed two processes, whereas the cation (**4a**) showed only one process, in accord with the ^{1}H n.m.r. observations. The two processes, relative to the reactions of cations (**1a**) and (**3a**), were largely separated. The faster process (relaxation time τ_1) led to the complete disappearance of the substrates. Therefore, if we take into account the n.m.r. patterns obtained under conditions of kinetic control, equations (1) and (2) hold for the cations

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

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

(**1a**) and (**3a**), respectively.* The slower process, which is independent of $[\mathrm{MeO}^-]$ (relaxation time τ_2), involves the equilibration of the two adducts through the intermediacy of the substrate, which is present in steady-state concentration. Therefore the application of the steady-state approximation to this process, according to Scheme 1, affords equations (3) and (4), for the cations (**1a**) and (**3a**), respectively.* The cation (**4a**) showed only one process, that led only to reversible formation of the 4*H*-adduct (**4b**); therefore equation (5) holds.

$$\tau_2^{-1} = \frac{k_2k_{-4} + k_4k_{-2}}{k_4} \qquad (3)$$

$$\tau_2^{-1} = \frac{k_2k_{-4} + k_4k_{-2}}{k_2 + k_4} \qquad (4)$$

$$\tau^{-1} = k_4[\mathrm{MeO}^-] + k_{-4} \qquad (5)$$

Some additional equilibrium measurements permitted the completion of our study. Since the cation (**1a**) is in equilibrium with both 2*H*- and 4*H*-adducts, we obtained the term $(K_2 + K_4)$. The cations (**2a**) and (**5a**) are only in equilibrium with the corresponding 2*H*-adducts, and therefore the equilibrium constants K_2 could be determined. These equilibrium measurements were carried out spectrophotometrically at very low methoxide ion concentration with chloroacetic acid–chloroacetate buffers in order to leave a detectable amount of the substrates in equilibrium with the adducts (see Experimental section).

The kinetic and equilibrium constants have been evaluated as follows: in the case of the cation (**1a**) the term $(K_2 + K_4)$, obtained spectrophotometrically, and the term K_4/K_2, obtained by ^{1}H n.m.r. measurements at 25 °C, were combined to give the equilibrium constants K_2 and K_4. A plot of τ_1^{-1} *vs.* $[\mathrm{MeO}^-]$ afforded k_4 [equation (1)], and therefore k_{-4} $(= k_4/K_4)$ could also be evaluated. From equation (3), since $K_2 = k_2/k_{-2}$, k_2 and k_{-2} were obtained. In the case of the cation (**2a**), k_4, k_{-4}, K_4, and k_2 were obtained in our previous work.[2] The equilibrium constant K_2 obtained spectrophotometrically allowed the evaluation of k_{-2} $(= k_2/K_2)$. In the case of the cation (**3a**) a plot of τ_1^{-1} *vs.* $[\mathrm{MeO}^-]$ afforded $(k_2 + k_4)$ [equation (2)]. This term in conjunction with k_4/k_2, obtained by ^{1}H n.m.r. measurements under conditions of kinetic control, allowed the evaluation of k_2 and k_4. The K_4/K_2 value $(= k_4k_{-2}/k_{-4}k_2)$, obtained by ^{1}H n.m.r. measurements under conditions of thermodynamic control, and equation (4) form a system of equations that could be solved for the unknowns k_{-2} and k_{-4}. In the case of cation (**4a**) a plot of τ^{-1} *vs.* $[\mathrm{MeO}^-]$ afforded k_4 and k_{-4} as slope and intercept, respectively. The K_4 value obtained from these kinetic constants is in good agreement with the value obtained from absorbance readings, carried out at the beginning (O.D.$_0$) and at the end (O.D.$_\infty$) of the reaction. Indeed at the monitoring wavelength only the substrate (**4a**) absorbs, and therefore equation (6) holds. The equilibrium constant

$$K_4 = (\mathrm{O.D.}_0 - \mathrm{O.D.}_\infty)/\mathrm{O.D.}_\infty\,[\mathrm{MeO}^-] \qquad (6)$$

K_2 for the cation (**5a**), that completes our previous kinetic investigation,[2] has been determined in the present work for reasons that will be made clear in the Discussion section. In Table 1 are reported the kinetic and equilibrium constants for the cations (**1a**)—(**6a**).

Discussion

Before discussing the present data we will recapitulate some of the principal conclusions drawn in our previous work dealing with methoxide attachment in MeOH to a series of 2,6-di-t-butyl-4-(substituted phenyl)-thiopyrylium[4] and -pyrylium[5] cations. It has been shown that, in spite of the large range of variation of the individual equilibrium constants K_2 and K_4 on changing the substituent on the phenyl group (both the constants span *ca.* 5 powers of 10 in the thiopyrylium series, and *ca.* 7 powers of 10 in the pyrylium series), K_2/K_4 remains substantially constant in each series (*ca.* 2×10^2 in the thiopyrylium series and *ca.* 2×10^4 in the pyrylium series). These results led us to the following conclusions: (i) the substituted phenyl group interacts only with the starting cation but not with the neutral 2*H*- and 4*H*-adducts;[4,5] (ii) the standard free energy difference between 2*H*- and 4*H*-adducts on exchanging sulphur with oxygen [equation (7)] is independent

$$\Delta\Delta G^\ominus = -RT\ln\left[\left(\frac{K_2}{K_4}\right)_{\mathrm{O}}\Big/\left(\frac{K_2}{K_4}\right)_{\mathrm{S}}\right] \qquad (7)$$

of the nature of the substituent on the phenyl ring ($\Delta\Delta G^\ominus = -11 \pm 1$ kJ mol^{-1}).[5] In fact we believe that the $\Delta\Delta G^\ominus$ value

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* Note that in the case of the cation (**1a**) equations (2) and (4) reduce to equations (1) and (3), respectively, because $k_4 \gg k_2$.

depends only on the nature of the two heteroatoms, because of the cancellation of ring substituent and solvent effects in the expression within square brackets in equation (7). The independence of $\Delta\Delta G^\circ$ from the substituents is now verified by the K_2/K_4 values for the cations (**2a**) and (**5a**) (from Table 1), which afford a $\Delta\Delta G^\circ$ value (-10.3 kJ mol^{-1}) in good agreement with the aforementioned $\Delta\Delta G^\circ$ value. The $\Delta\Delta G^\circ$ value can be used to predict the $(K_2/K_4)_S$ value, if the $(K_2/K_4)_O$ in the same solvent is known, and *vice versa*. Therefore from the K_2/K_4 value for the cation (**6a**) (from Table 1) we can estimate a K_2/K_4 value of $(1.3 \pm 0.5) \times 10^{-2}$ for the cation (**4a**) that in turn allows the estimation of the equilibrium constant K_2 (see Table 1). The low value of K_2/K_4 is consistent with the non-detection of the 2*H*-thiopyran (**4c**) by ^{1}H n.m.r.

There is a good correlation between the log K_2 values of the thiopyrylium cations (**1a**)—(**4a**) and the $\sigma_p{}^+$ values of the corresponding substituents ($\rho = 5.4$; $r = 0.999$) (not shown). It is interesting to compare this ρ value with that obtained for methoxide addition to the α-position of 2,6-di-t-butyl-4-(substituted phenyl)thiopyrylium cations ($\rho = 2.0$).[4] As expected a higher ρ value is observed for the cations (**1a**)—(**4a**) with the γ-substituents directly attached to the thiopyrylium ring.

Now we turn our attention to the problem of the *ipso*-effects. In the case of X-substituted aromatic substrates *ipso*-attack is defined as the attack of a given reagent Y at the X-substituted carbon atom. The *ipso*-effect is due to the interactions between the geminal groups Y and X. In order to separate the Y–X *ipso*-effect from the other factors affecting the free energy change of a given reaction, this term must be compared with the free energy change of the reference reaction in which this effect is zero by definition, *i.e.* that in which X = H. For example in the case of the formation of negatively charged Meisenheimer adducts, *ipso*-effects were evaluated by equation (8),[1] where K^X is the

$$\Delta\Delta G^\circ = -RT\ln(K^X/K^H) \qquad (8)$$

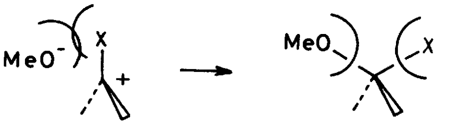
stability constant of the adduct obtained by nucleophilic attack on the *ipso*-position of the X-substituted substrate, and K^H is the corresponding equilibrium constant when X = H. Such an estimation of *ipso*-effects is based on the assumption that $\Delta\Delta G^\circ$ is essentially a reflection of the difference in the free energies of the negatively charged adducts; in other words it is assumed that the group X negligibly affects the free energy of the neutral substrate. This assumption can be justified if we consider that electronic substituent effects play a significant role only on charged species. Since thiopyrylium cations are positively charged substrates, we cannot neglect the electronic effect of the group X on the substrate (*cf.* the Brown–Okamoto relationship previously indicated). Therefore in our case we propose to base the measure of the *ipso*-effects on the equilibrium constant of the isomerisation of the 4-X-substituted 2*H*-adduct to the 4*H*-isomer, $(K_4/K_2)^X$, referred to the corresponding equilibrium constant when X = H, $(K_4/K_2)^H$ [equation (9)]. This proposal

$$\Delta\Delta G^\circ = -RT\ln(K_4/K_2)^X/(K_4/K_2)^H \qquad (9)$$

relies on the assumption that the free energy of the 2*H*-adduct is negligibly affected by the electronic effect of the substituent X in the 4-position. Indeed for both the series of 2,6-di-t-butyl-4-(substituted phenyl)-thiopyrylium[4] and -pyrylium[5] cations, where the γ *ipso*-effect can be considered constant, K_4/K_2 does not change on changing the electronic effect of the substituted phenyl ring.

Since for the reference cation (**1a**) (X = H) $K_4/K_2 \simeq 1$, equation (9) simplifies to (10). In the case of the cation (**3a**)

$$\Delta\Delta G^\circ = -RT\ln(K_4/K_2)^X \qquad (10)$$



Scheme 2.

(X = Bu^t), K_4 is similar to K_2, thus indicating a negligible *ipso*-effect, which excludes significant steric interactions between the geminal OMe and Bu^t groups in the 4*H*-adduct (**3b**). Some sensitivity of bulky groups to *ipso*-effects has also been noted elsewhere (in an admittedly different case), *viz.* the brominative electrophilic attack on the *para*-position of phenols.[6] In fact in this reaction, the transition-state structure for which is very similar to the σ-adduct, the *ipso*-reactivity was found to change slightly in going from hydrogen to methyl to t-butyl.

In the case of the cation (**4a**), K_4 must be corrected for the statistical factor, in order to make the comparison with K_2 (*i.e.* $K_4{}^c = K_4 \times 2$). Since $K_4{}^c/K_2 \simeq 1.5 \times 10^2$, the stabilising effect of the *gem*-dimethoxy substitution can be estimated as *ca.* 12 kJ mol^{-1}. The stabilising effect of the multiple alkoxy substitution on an sp^3 carbon atom, first recognised by Hine,[7] has been extensively taken into account to explain the higher stabilities of *gem*-dialkoxy Meisenheimer adducts with respect to monoalkoxy analogues.[1] An attempt to estimate the effect of *gem*-dimethoxy substitution from data referring to the stability of Meisenheimer adducts led to a value of *ca.* 10 kJ mol^{-1},[1,8] which, corrected for the statistical factor, yields a value (*ca.* 11.7 kJ mol^{-1}) in excellent agreement with our estimation.

The K_4/K_2 value for the cation (**2a**) (*ca.* 1.5×10^{-2}) reveals a quite unexpected destabilisation (*ca.* 10 kJ mol^{-1}) of the geminal OMe and Ph groups in the γ-position. This effect could hardly be attributed to steric interactions, since these are negligible in the presumably more crowded 4*H*-adduct (**3b**). At present we have no convincing explanation for such a destabilising effect; nevertheless we suggest that it may originate from some electronic repulsion between the π-system of the phenyl and the lone pairs of the geminal methoxy group.

We note that the k_2 values for the cations (**1a**)—(**3a**) decrease in the same order as the equilibrium constants K_2, though less markedly, as expected for a well behaved rate–equilibrium relationship. However the kinetic constants k_4 do not follow the same trend as the equilibrium constants K_4. The k_4 sequence (H > OMe > Ph > Bu^t), being the same as that for the corresponding hindrances,[9] suggests the involvement of steric effects in the transition state. The present data, however, are as yet too limited to allow a quantitative appraisal of such effects.

Nevertheless the presence of steric interactions in the transition states yielding the 4*H*-adducts and their absence in the final 4*H*-adducts indicate that the structure of the activated complex significantly differs from that of the γ-product. We suggest that the greater crowding of the transition state can be ascribed to a nearly sp^2 hybridisation at carbon, as depicted in Scheme 2. This description implies an ion-pair-like transition state, and indeed such a hypothesis, on different grounds[3,4] has already been suggested for this class of reactions.

Experimental

Materials.—[^{2}H$_4$]Methanol for n.m.r. spectroscopy was obtained from Merck. Dry methanol was obtained as previously reported.[10] Stock solutions of sodium methoxide were prepared by dissolving the appropriate amount of clean sodium in methanol (or deuteriated methanol) under argon. Methanolic HClO$_4$ was prepared by a published procedure.[11] Purification of triethylamine and preparation of triethylamine–triethylammonium buffers were carried out as previously indicated.[10]

Table 2. Observed kinetic constants for the reactions of the cations (**1a**), (**3a**), and (**4a**) with methoxide ion in MeOH at 25 °C

Substrate	$[MeO^-]$ / M	τ_1^{-1} / s^{-1}	τ_2^{-1} / s^{-1}
(**1a**)[a]	3.60×10^{-8}	1.63	5.76×10^{-4}
	5.76×10^{-8}	2.12	5.65×10^{-4}
	8.23×10^{-8}	2.86	5.78×10^{-4}
	1.44×10^{-7}	4.51	5.68×10^{-4}
	2.88×10^{-7}	8.34	5.74×10^{-4}
	5.76×10^{-7}	15.9	5.72×10^{-4}
(**3a**)[b]	2.55×10^{-4}	35.2	1.35×10^{-3}
	3.82×10^{-4}	47.6	1.35×10^{-3}
	4.58×10^{-4}	67.0	1.37×10^{-3}
	5.10×10^{-4}	70.7	1.38×10^{-3}
	6.10×10^{-4}	88.6	1.36×10^{-3}
	8.00×10^{-4}	111	1.39×10^{-3}
	8.92×10^{-4}	127	1.37×10^{-3}
	1.02×10^{-3}	146	1.39×10^{-3}
(**4a**)[a,c]	2.54×10^{-7}	1.33	
	3.18×10^{-7}	1.53	
	6.35×10^{-7}	2.61	
	1.27×10^{-6}	4.73	
	2.54×10^{-6}	8.60	

[a] With $Et_3N–Et_3NH^+$ buffers, at constant $[Et_3NH^+] = 5.00 \times 10^{-3}$M. [b] With sodium methoxide solutions. [c] Only one process.

Chloroacetic acid (Aldrich Gold Label) was used without further purification. Chloroacetic acid–chloroacetate buffers were prepared by partial neutralisation of the acid with sodium methoxide solutions.

2,6-Diphenylthiopyrylium (**1a**), 2,4,6-triphenylthiopyrylium (**2a**), 2,6-diphenyl-4-methoxythiopyrylium (**4a**), and 2,4,6-triphenylpyrylium (**5a**) perchlorates were available from our previous work.[3]

2,6-*Diphenyl*-4-*t-butylthiopyrylium perchlorate* (**3a**) was obtained by treating 2,6-diphenyl-4-t-butylpyrylium perchlorate[3] with sodium sulphide in aqueous acetone according to the procedure described by Mislow and co-workers for (**2a**).[12] Owing to the presence of a little of the starting pyrylium salt in the product mixture, this was treated with sodium sulphide in aqueous acetone for a second time, thus affording the pure thiopyrylium salt (**3a**) in 42% overall yield; m.p. 252—253 °C (Found: C, 62.5; H, 5.2. $C_{21}H_{21}ClO_4S$ requires C, 62.3; H, 5.2%); δ(CD_3OD) 1.65 (9 H, s, 4-Bu^t), 7.8—8.2 (10 H, m, 2- and 6-Ph), and 8.94 (2 H, s, 3- and 5-H).

^1H *N.m.r. Measurements*.—The ^1H n.m.r. measurements were carried out with a Bruker WP 80 SY spectrometer. Low-temperature (−40 °C) and room-temperature (25 °C) ^1H n.m.r. measurements for the reaction of the cation (**3a**) with CD_3ONa in CD_3OD were carried out according to the procedure previously described.[3] The adducts (**3b**) and (**3c**) showed δ (**3b**) 1.02 (9 H, s, 4-Bu^t), 5.96 (2 H, s, 3- and 5-H), and 7.2—7.6 (m, 2- and 6-Ph); δ (**3c**) 1.29 (9 H, s, 4-Bu^t), 5.35 (1 H, d, *J* 0.7 Hz, 3-H), 6.80 (1 H, d, *J* 0.7 Hz, 5-H), and 7.2—7.6 (m, 2- and 6-Ph).*

Rate Measurements.—Kinetic experiments were carried out with a Durrum 110 stopped-flow spectrophotometer or a Cary 219 spectrophotometer at 25.0 °C under pseudo-first-order conditions with MeONa or $Et_3N–Et_3NH^+$ buffer. The methoxide ion concentration of each buffer was calculated from the pK_a value of Et_3N (10.88)[11] and from the methanol autoprotolysis constant (pK_{MeOH} = 16.92).[13] Substrate concentrations were in the range (1—4) × 10^{-5}M. The reaction solutions were freshly prepared and handled under argon. In the case of cations (**1a**) and (**3a**) two largely separate first-order processes were observed; kinetic constants (τ_1^{-1} and τ_2^{-1}) were obtained by first-order standard treatment of the two processes. The kinetics were monitored at wavelengths where the largest absorbance variations occur: (**1a**) 404 (τ_1) and 325 (τ_2); (**3a**) 394 (τ_1) and 318 (τ_2); (**4a**) 360 nm. Typical errors in τ_1^{-1} and τ_2^{-1} are ±4%.

The experimental data are reported in Table 2.

Equilibrium Measurements.—The equilibrium constants which could not be evaluated from kinetic and ^1H n.m.r. experiments were determined spectrophotometrically at 25.0 °C, by measuring the residual absorbance of the substrate (O.D.$_\infty$) after equilibration with chloroacetic acid–chloroacetate buffer solutions. Such measurements were carried out for cations (**1a**), (**2a**), and (**5a**) at wavelengths 420, 400, and 410 nm, respectively, where only the substrate absorbs. The addition of an excess of methanolic $HClO_4$ to these mixtures shifts the equilibrium completely toward the substrate, thus permitting the measurement of O.D.$_0$ after correction of the observed O.D. value for dilution. In the case of the cations (**2a**) and (**5a**), the 2*H*-adduct being the only final product, we obtain equation (11).

$$K_2 = (OD_o - OD_\infty)/O.D._\infty\,[MeO^-] \qquad (11)$$

Since cation (**1a**) reacts with methoxide ion to give a mixture of the 2*H*- and 4*H*-adducts, we obtain equation (12).

$$K_2 + K_4 = (OD_o - OD_\infty)/O.D._\infty\,[MeO^-] \qquad (12)$$

The methoxide ion concentration of each buffer was calculated from the pK_a of chloroacetic acid (7.7)[14] and from the methanol autoprotolysis constant (see before). The ionic strength was always lower than 3.00 × 10^{-3}M. The concentration of the substrates was in the range (1—4) × 10^{-5}M. The measurements were carried out with a Cary 219 spectrophotometer, with Teflon-stoppered 1 cm quartz cells.

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* The superimposition of the phenyl group signals of the 2*H*- and 4*H*-adducts does not allow integral evaluation.