concentrated to ca. 3 mL, and then 10 mL of methanol was added. The formed precipitates were collected, and recrystallization from hot methanol–benzene gave colorless crystals of **7f′** (0.35 g, 15%). The solvent of the filtrate was evaporated, and the residual solid was extracted with 10 mL of ether–benzene (1:1) and the extract filtered. The filtrate was concentrated to ca. 1 mL, and the recrystallization of the formed precipitates from methanol gave 0.24 g (15%) of **7f**. The yield of **7f′** increased when the mole ratio of **2f**/**3** was 1:2. A mixture of **6** (0.26 g, 0.24 mmol), **2f** (0.92 g, 5 mmol), benzene (5 mL), and **3** (1.42 g, 10 mmol) was heated in a sealed tube at 100 °C for 8 h. The reaction mixture was allowed to stand at room temperature overnight. Recrystallization of the formed colorless crystals from benzene–methanol (3:2) gave 1.26 g (54%) of **7f′**. From the filtrate, **7f** could not be isolated. **7f**: mp 110–111 °C; IR (KBr) 3065, 1735, 1710, 1625 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 5.97 (m, 2 H, olefinic), 3.77 (s, 6 H, OMe), 2.64 (m, 2 H), 2.58 (s, 2 H), 2.15 (s, 2 H), 1.78, 1.22 (AB q, 2 H, J = 8.5 Hz, bridge), 1.70, 1.21 (AB q, 2 H, J = 11.5 Hz, bridge), 1.48 (s, 4 H, cyclobutane). Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.03; H, 6.98. **7f′**: mp 259–260 °C; IR (KBr) 1730, 1708, 1630 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.77 (s, 12 H, OMe), 2.53 (s, 4 H, *endo*-cyclobutene), 2.13 (s, br, 4 H, bridgehead), 1.70 (s, 4 H, cyclobutane), 1.60 (AB q, J = 11.4 Hz, 4 H, bridge); mol wt (cryoscopic in benzene) 420 (468.5). Anal. Calcd for $C_{26}H_{28}O_8$: C, 66.67; H, 6.02. Found: C, 66.46; H, 6.02.

Dimethyl 7,8-benzo-8-oxatricyclo[4.2.1.0^{2,5}]non-3-ene-3,4-dicarboxylate (7g) was prepared from **2g** (10 mmol) and **3** (10 mmol) in the same manner used in the preparation of **7e** (yield 59%). **7g**: mp 151–152 °C; IR (KBr) 1731, 1714, 1638 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 7.23 (m, 4 H, Ph), 5.16 (s, 2 H, bridgehead), 3.83 (s, 6 H, OMe), 2.93 (s, 2 H, endo); MS m/e 286, 255, 227. Anal. Calcd for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 66.92; H, 4.95.

Tetramethyl 7-oxa-*exo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene-3,4,7,8-tetracarboxylate (7h) was prepared from **2h** (10 mmol) and **3** (10 mmol) in the same manner used in the preparation of **7e** (yield 21%). **7h**: mp 160–161 °C (lit.[30] mp 157–158 °C); IR and ^1H NMR spectra were identical with those reported.[30] Anal. Calcd for $C_{16}H_{16}O_9$: C, 54.55; H, 4.58. Found: C, 54.53; H, 4.38.

Tetramethyl 1-methyl-7-oxa-*exo*-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene-3,4,7,8-tetracarboxylate (7i) was prepared in the same manner described above: yield 10%; mp 102–103 °C; IR (KBr) 1730, 1715, 1633 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 5.03 (s, 1 H, bridgehead), 3.87 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 3.10 (s, 2 H, endo), 1.63 (s, 3 H, Me); MS m/e 366, 335. Anal. Calcd for $C_{17}H_{18}O_9$: C, 55.74; H, 4.95. Found: C, 55.91; H, 4.92.

Reaction of Furan Derivatives or Cyclopentadiene with 3. The reaction of furan is representative. A mixture of **6** (0.11 g, 0.10 mmol), benzene (5 mL), furan (0.36 mL, 5 mmol), and **3** (1.42 g, 10 mmol) was heated in a sealed tube at 100 °C for 6 h. The solvent of the reaction mixture was evaporated, and the formed precipitates were collected on a glass filter and washed with a small amount of methanol. Recrystallization from methanol gave colorless crystals of **7h** (yield 1.29 g, 73%). The reaction of 2-methylfuran or cyclopentadiene with **3** was carried out similarly. Yields of the products were summarized in Table II.

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Registry No. **1**, 19529-00-1; **2a**, 498-66-8; **2b**, 121-46-0; **2c**, 39589-98-5; **2d**, 4453-90-1; **2e**, 947-57-9; **2f**, 1624-12-0; **2g**, 573-57-9; **2h**, 1829-60-3; **2i**, 18064-04-5; **3**, 762-42-5; **4**, 25360-32-1; **5**, 71901-90-1; **6**, 71901-91-2; **7a**, 5063-02-5; **7b**, 13155-83-4; **7b′**, 71928-61-5; **7c**, 61697-17-4; **7d**, 61697-16-3; **7e**, 20180-47-6; **7f**, 71901-86-5; **7f′**, 71901-87-6; **7g**, 71928-62-6; **7h**, 17732-05-7; **7i**, 71901-88-7; **12e**, 542-92-7; **12h**, 110-00-9; **12i**, 534-22-5; dimethyl dihydro-*cyo*-tricyclo-[4.2.1.0^{2,5}]non-3-en-3,4-dicarboxylate, 71901-89-8; $C_6(CO_2Me)_6$, 6237-59-8.

Rates and Equilibria for the Addition of Methoxide Ion to 2,6-Diphenyl- and 4-Methoxy-2,6-diphenylpyrylium Cations

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The reactions of addition of MeO^- to the title cations, **1** and **2**, respectively, have been studied spectrophotometrically in MeOH. Owing to the high reactivity of these cations, buffers have been used for the kinetic measurements. The system Et_3N/Et_3NH^+ has been found suitable because of the low reactivity of Et_3N toward the substrates. Rate and equilibrium constants for the addition to position 4 of **1** and to positions 2 and 4 of **2** have been determined or estimated at 25 °C. The equilibria are well shifted toward the adducts, much more than in the additions of MeO^- to N-substituted pyridinium cations. The lower rate of addition to the methoxy-bearing position of **2** with respect to that of addition to the hydrogen-bearing position of **1** is discussed in terms of electronic and other structural effects and also in comparison with related data for the addition to the trinitrobenzene and dinitrothiophene systems.

The formation of anionic σ adducts (Meisenheimer adducts) from neutral, suitably substituted aromatic molecules and negatively charged nucleophiles has been intensively investigated in physical organic studies.[1] Quantitative work has also been carried out in more recent years with similar adducts from heteroaromatic six- and five-membered ring substrates.[2-4]

Adduct formation may also occur in reactions of a different charge type, such as the ones involving cationic substrates, and negatively charged nucleophiles to give

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(1) For relevant reviews, see: Foster, R.; Fyfe, C. A. *Rev. Pure Appl. Chem.* **1966**, *16*, 61. Buncel, E.; Norris, A. R.; Russell, K. E. *Q. Rev., Chem. Soc.* **1968**, *22*, 123. Crampton, M. R. *Adv. Phys. Org. Chem.* **1969**, *7*, 211. Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667. Fyfe, C. A. In "The Chemistry of the Hydroxyl Group"; Patai, S., Ed.; Interscience: New York, 1971.

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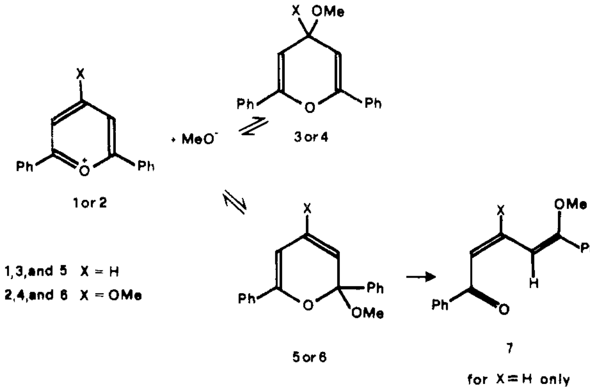
0022-3263/79/1944-4496$01.00/0

Scheme I



neutral σ adducts.[5] The kinetics and equilibria of pseudobases and related adducts from quaternized N-heteroaromatics have received considerable attention,[6,7] but much less is known of the reactivity of pyrylium ions, except for the hydrolysis of 4-ethoxypyrylium salts.[8]

In this paper we wish to contribute to fill this gap by the study of the reactivities of 2,6-diphenylpyrylium (**1**) and 4-methoxy-2,6-diphenylpyrylium (**2**) ions toward methoxide ion in methanol solution at 25 °C. The course of these reactions in methanol and acetonitrile–methanol (9:1, v/v) has already been reported in a previous paper[9] together with the structural assignments of the adducts formed (Scheme I).

One of the aims of our studies is to obtain a better understanding of the factors involved in the dynamics of σ-adduct formation. The extent of delocalization of the positive charge in the heteroaromatic ring is certainly one such factor. Another structural feature of cations **1** and **2** is that one of the possible reactive positions (at carbon 4) is flanked by hydrogen atoms and is less subject to steric hindrance on the approach of the attacking nucleophile. Varying degrees of hindrance are experienced by neutral six- and five-membered ring systems because of the unavoidable presence of activating substituents such as the nitro group. Evidence was set forth[2] that F-strain may play a role in determining the reactivity of a benzene ring at a methoxyl-bearing position when flanked by two nitro groups. With pyrylium ions as reference substrates, further information can hopefully be obtained on the relative importance of structural factors in adduct formation.

Results

Owing to the high reactivity of pyrylium cations **1** and **2** toward the methoxide ion, the determination of rate and equilibrium constants turned out to be impractical in methoxide ion solutions, no matter how dilute, as prepared from stock solutions. Such data could, however, be obtained by using buffer systems.

2,6-Diphenylpyrylium Cation (1). As reported previously,[2] the reaction of **1** with sodium methoxide leads to two products, the 4*H*-pyran **3** and the open-chain dienone **7**. The former is formed first under kinetic control, while the latter is formed more slowly under thermodynamic control. The relative rate of appearance of these products is such as to make their formation quite distinguishable kinetically. Attempts to determine reaction rates at room temperature with MeONa concentrations as low as 10^{-5} M failed because the disappearance of the 400-nm absorption maximum of **1** was too fast to be measured under stopped-flow conditions.

Table I. Rate Constants for the Reaction of 1 with $PhCO_2^-/PhCO_2H$ Buffers in Methanol at 20 °C

A. At Varying MeO^- Concentration[a]

$PhCO_2^-/PhCO_2H$	$10^7[CH_3O^-]$, M	k_{obsd}, s^{-1}
12.5	2.9	50
8.3	1.9	43
6.3	1.45	38
5.0	1.2	35.5

B. At Constant MeO^- Concentration[b]

$10^4[PhCO_2^-]$, M	k_{obsd}, s^{-1}
4.0	16
12	20
20	22
100	43

[a] $[PhCO_2^-] = 0.01$ M. $k_{MeO^-} = 8.95 \times 10^7\ M^{-1}\ s^{-1}$.
[b] $[MeO^-] = 1.9 \times 10^7$ M. $k_{PhCO_2^-} = 2.77 \times 10^3\ M^{-1}\ s^{-1}$.

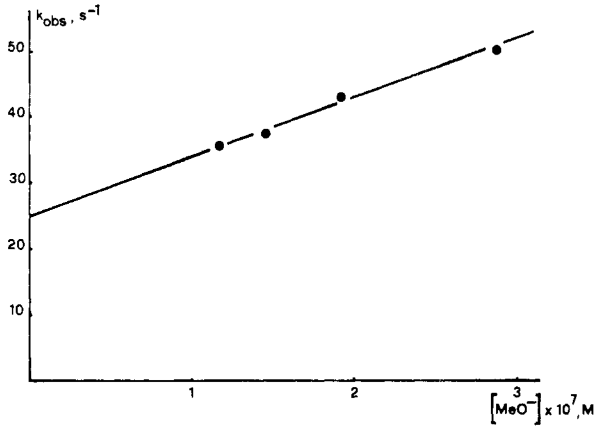


Figure 1. Plot of observed pseudo-first-order rate constant for the reaction of 1 with MeO^- at constant $[PhCO_2^-]$ at 20 °C.

Rate data for the formation of **3** were obtained in the presence of such buffer systems as sodium benzoate/benzoic acid and triethylamine/triethylammonium perchlorate, which upon methanolysis yielded the required very low concentrations of methoxide ion (see Experimental Section). As a consequence, the reaction rates became low enough so as to permit the measurements by the stopped-flow technique. The early part of the measurements for benzoate/benzoic acid and other herein unreported buffers was carried out at 20 °C, rather than at 25 °C, because of the availability of the several relevant pK_a values at suitable ionic strength at that temperature.

With the benzoate buffer, the observed pseudo-first-order rate constants (Table I) were found to be dependent on both methoxide and benzoate ions (eq 1).

$$k_{obsd} = k_{MeO^-}[MeO^-] + k_{PhCO_2^-}[PhCO_2^-] \qquad (1)$$

When the observed rate constant, k_{obsd}, was plotted as a function of $[MeO^-]$ at constant benzoate concentration (Figure 1) and of $[PhCO_2^-]$ at constant $[PhCO_2^-]/[PhCO_2H]$ ratio (Figure 2), the respective rate constants, k_{MeO^-} and $k_{PhCO_2^-}$, were obtained from the slopes. Since $k_{MeO^-} \gg k_{PhCO_2^-}$, the contribution of the methoxide ion term is important even at relatively high benzoate ion concen-

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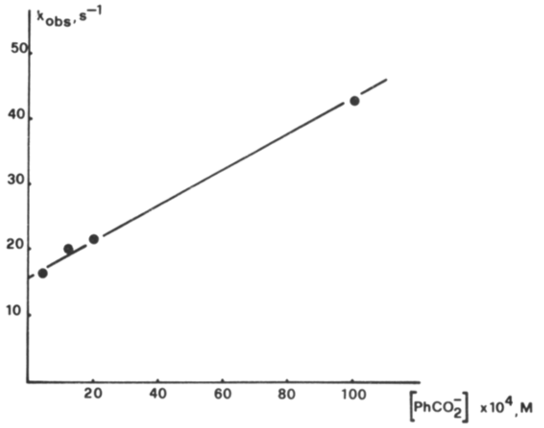

Figure 2. Plot of observed pseudo-first-order rate constant for the reaction of 1 with MeO^- at constant $[MeO^-]$ and variable $PhCO_2^-$ at 20 °C.

Table II. Rate Constants for the Reaction of 1 with Methoxide Ion in Methanol[a]

$10^4[Et_3N]$, M	$10^7[MeO^-]$, M	k_{obsd}, s^{-1}
5.8	1.3	28.7
9.9	2.3	42.7
16	3.7	59.9
21	4.8	75.4
40	9.0	119
70	16.1	204

[a] At 25 °C in the presence of Et_3N/Et_3NH^+ buffers ($[Et_3NH^+] = 4 \times 10^{-3}$ M). $k_{MeO^-} = 1.17 \times 10^8$ M^{-1} s^{-1}. $k_{MeOH} = 0.64$ M^{-1} s^{-1} (intercept at 15.9 s^{-1}).

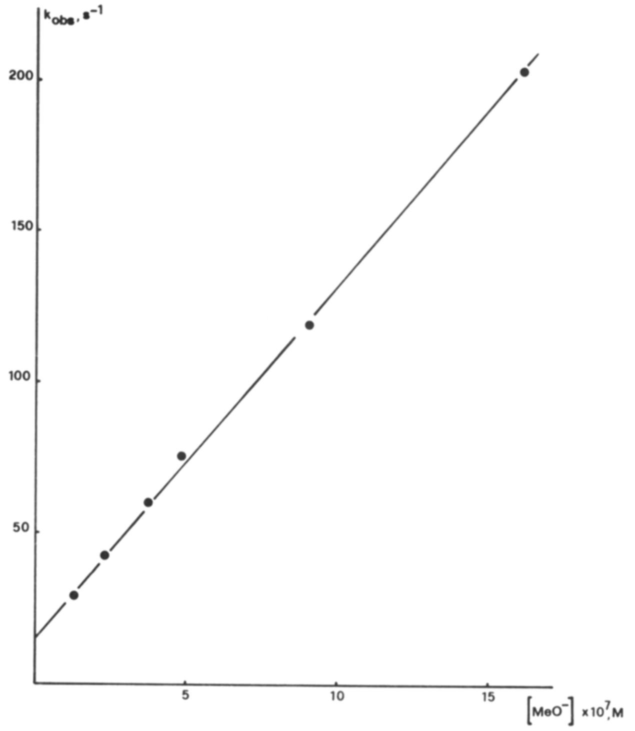

Figure 3. Plot of observed rate constant for the reaction of 1 with MeO^-, with Et_3N/Et_3NH^+ buffers, at 25 °C.

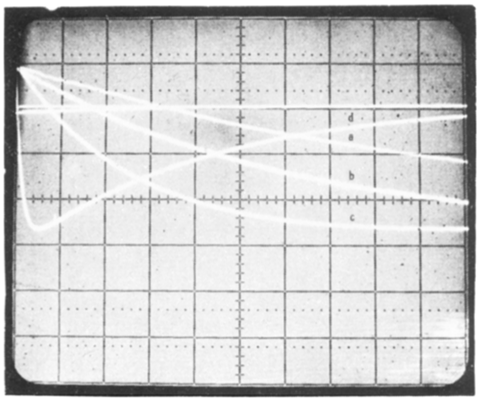

Figure 4. Oscilloscope trace at 320 nm for the reaction of 2 (4.0×10^{-5} M) with MeO^- (4.9×10^{-6} M) ($[Et_3N] = 5.4 \times 10^{-3}$ M, $[Et_3NH^+] = 10^{-3}$ M) at 25 °C. (a) 10 ms/div; (b) 20 ms/div; (c) 50 ms/div; (d) 1 s/div. Vertical scale: 0.1 abs/div.

trations. The benzoate term may consist of either a direct nucleophilic attack of the substrate by the benzoate ion or a general-base-catalyzed attack by the solvent. We have not ascertained this point.

When the triethylamine buffer was used, the observed pseudo-first-order constants that are reported in Table II were obtained at varying methoxide ion concentrations by keeping the triethylammonium ion concentration constant and changing the concentration of triethylamine. They were found to be linearly dependent on the calculated methoxide ion concentration (Figure 3). The tertiary amine gives no contribution to the observed rate constant since a change in concentration of the components of the buffer, at a fixed triethylamine/triethylammonium ratio, did not affect the reaction rate. Accordingly, the k_{MeO^-} value of 1.1×10^8 M^{-1} s^{-1} at 25 °C, as obtained from the slope, is in satisfactory agreement with the k_{MeO^-} value derived from the benzoate buffer experiments at 20 °C, allowance being made for the difference in temperature. Owing to the very high reactivity of the substrate, the rate measurements were only made in a narrow range of methoxide ion concentrations. This prevented the drawing of a rate profile as a function of the acidity of the medium extensively enough so as to work out a more detailed kinetic analysis. Indeed, noncatalytic as well as catalytic terms for both forward and reverse reactions have been unveiled in the case of the analogous pseudobase formation from quaternized N-heteroaromatic compounds.[6] Nevertheless, from the intercept of the plot reported in Figure 3 (see also Table II) it was possible to evaluate the rate constant for the attack by the solvent, $k_{MeOH} = 0.64$ M^{-1} s^{-1}. Being relatively small, this value was neglected to a first approximation.

4-Methoxy-2,6-diphenylpyrylium Cation (2). A general time-dependent UV spectral pattern was obtained from experiments carried out with Et_3N/Et_3NH^+ buffers, yielding $[MeO^-] = 10^{-5}$–10^{-6} M. The reaction was followed by the stopped-flow technique, in the 320–360-nm range, where the substrate and the 2*H*-pyran **6** are known to absorb. The reaction occurs in two subsequent main stages, as illustrated by a typical oscilloscope trace recorded at 320 nm, where the absorbance is spanned in four different time scales (Figure 4). In the former stage the absorbance decreases rapidly at a rate which is methoxide ion dependent; in the latter stage the absorbance increases again and reaches a constant value in nearly 10 s. In the last portion of this process the rate of the change in absorbance becomes independent of the MeO^- concentration.

Since the molar absorptivity coefficient of 2*H*-pyran **6** at 320 nm is higher than that of the substrate, the initial decrease in absorbance has been attributed to the prevailing formation of the 4*H*-adduct **4**, which is characterized by a low absorptivity at this wavelength. The subsequent slow increase in absorbance can be related to a slow increase in the concentration of the 2*H*-pyran at the expense of that of the 4*H*-pyran and, eventually, to the equilibration between the two.

Table III. Rate and Equilibrium Constants for the Reaction of 4-Methoxy-2,6-diphenylpyrylium Ion (2) To Give 2*H*- and 4*H*-Pyrans 6 and 4[a]

$k_4 = 3.15 \times 10^6\ M^{-1}\ s^{-1}$ $k_6{}^b = 5.05 \times 10^5\ M^{-1}\ s^{-1}$
$k_{-4} = 0.94\ s^{-1}$ $k_{-6} = 0.138\ s^{-1}$
$K_4{}^c = 3.35 \times 10^6\ M^{-1}$ $K_6{}^c = 3.65 \times 10^6\ M^{-1}$

[a] In methanol in the presence of Et_3N/Et_3NH^+ buffers at 25 °C. [b] Uncorrected for the statistical factor. [c] Equilibrium constants obtained spectrophotometrically were $K_4 = (3.1 \pm 0.2) \times 10^6\ M^{-1}$ and $K_6 = (3.4 \pm 0.2) \times 10^6\ M^{-1}$.

A detailed kinetic study was carried out in the presence of Et_3N/Et_3NH^+ buffers, where the observed reaction pattern is in agreement with eq 2 (see Experimental Section). The computer-assisted fitting of the experimental data allowed us to obtain the rate constants reported in Table III.

$$2H\text{-pyran } \mathbf{6} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \text{substrate } \mathbf{2} + \text{MeO}^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} 4H\text{-pyran } \mathbf{4} \qquad (2)$$

As with the reaction of 1, it was ascertained that a change in concentration of the buffer, at a fixed methoxide ion concentration, did not affect the reaction rate. A study with the benzoate buffer was not undertaken, because of the possibility that both benzoate and methoxide ions are involved in the process, giving rise to a more complicated kinetic picture.

Discussion

With both substrates 1 and 2 the reaction under kinetic control is the one involving attack of the nucleophile at position 4 to give 4*H*-pyrans 3 and 4, respectively. With 1 it was not possible to determine the reactivity of position 2 because the expected 2*H*-pyran 5 is not observed, and the open-chain dienone 7 is obtained instead. Presumably, 3 tends to equilibrate slowly with 5 via return to 1, and then 5 converts into 7 in a fast step.

The reactivity of the pyrylium cation 2 at position 4 is higher than that at position 2 by about one order of magnitude. However, this reactivity ratio is not likely to reflect the relative inherent reactivities of the pyrylium cation at positions 2 and 4, owing to the presence of the substituents. In particular, the presence of a phenyl group at the α position is expected to appreciably hinder the approach of the nucleophile and, therefore, to exert a rate-depressing effect. As a whole, the reactivities of both cations are very high, the rate constants ranging from 10^5 to 10^8, and, especially for the formation of 3, nearly approach the level known for diffusion-controlled processes. Although the complications arising from the ambident character of these cations and, in one instance, from ring-opening decomposition make a test of N_+ correlations difficult, it is of interest that their reactivity levels are comparable to those found by Ritchie for the combination of other organic cations with negatively charged nucleophiles.[10]

The equilibrium constant for the formation of 3 (K_3) was only roughly estimated because, when the concentration of 3 reaches its highest value, a low residual absorbance at the wavelength characteristic for an absorption maximum of the starting pyrylium cation (400 nm) is recorded and found to be independent of the concentration of methoxide ion. This suggests that such an absorbance is unlikely to be due to any residual free pyrylium cation. However, even on the assumption that the residual absorbance was due to 1, the K_3 value is estimated to be greater than $10^7\ M^{-1}$.

Table IV. Comparison of the Rate of Addition to Hydrogen- and Methoxyl-Bearing Positions

series	k_H/k_{OMe}
1-X-2,4,6-trinitrobenzene	4.1×10^2
2-X-3,5-dinitrothiophene	0.4
4-X-2,6-diphenylpyrylium	37

The equilibrium constants for the formation of 4 and 6 from 2 are also very high. So there is noted a general, though not exact, correspondence between rates and equilibria (Table III).

It is worth comparing the behavior of the pyrylium cations 1 and 2 with that of 1-arylpyridinium cations in the formation of 1,2-dihydropyridines[11] under similar reaction conditions. Although the two types of cationic systems are not strictly comparable because they are differently substituted, they display such a great difference in equilibrium constant values for the reaction with methoxide ion that the nature of the charged heteroaromatic ring is held mainly responsible. The value for the formation of 1-phenyl-2-methoxy-1,2-dihydropyridine from the 1-phenylpyridinium ion is 1.7 M^{-1} at 25 °C, which is smaller than the above values for the reactions of pyrylium cations by a factor of 10^6 or more. Such a difference may presumably reflect a greater cationic character of the carbon ring positions 2 and 4 in the pyrylium ion as compared to those of the pyridinium system, in line with the extensive delocalization of the positive charge and the weak residual charge at the oxygen atom of the pyrylium cation as found in recent calculations by diverse methods.[12,13]

The present data have a bearing on the assessment of the factors responsible for the influence on reaction rate of substituent X (H, OMe) attached to the ring carbon undergoing the addition of the methoxide ion. To illustrate this point, we compared the k_H/k_{MeO} value for the 4-X-2,6-diphenylpyrylium ions to the ones reported for 1-X-2,4,6-trinitrobenzenes[14] and 2-X-3,5-dinitrothiophenes[2] (Table IV). Most early studies have concentrated on the trinitrobenzene system where four factors can be assumed to play a role in determining the reactivity of the substrate when X = OMe, as compared to when X = H. Such factors include F-strain,[2,15] steric inhibition of resonance (SIR) of the nitro groups adjacent to X = OMe,[14] the bond-strengthening conjugation of X = OMe with the aromatic ring,[14] and the geminal dimethoxy effect.[14] The former three are rate-depressing factors for X = OMe and will tend to exalt the k_H/k_{OMe} ratio, whereas the latter is a rate-enhancing factor which will contribute to lower the k_H/k_{OMe} ratio. The markedly high ratio found for the benzene system (410) suggests that the rate-depressing factors are quite important in such a case. In going to the thiophene system, both F-strain and SIR effects should be far less important because there is only one nitro group flanking the OMe substituent, and its coplanarity with the ring is facilitated by the pentagonal geometry of the ring.[16] With this system the opposing factors are fortuitously balanced, the ratio being 0.4. However, in going to the pyrylium case, the ratio rises appreciably again (37) despite the fact that the OMe group is flanked by hydrogens only

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and that no SIR effect can occur. Thus, here we have a genuine case of retardation as exclusively caused by the ground-state stabilization of the substrate (p–π conjugation). Clearly an effect of this kind cannot be singled out in the overcrowded 2,4,6-trinitroanisole.

Experimental Section

Materials. Perchlorates of 1 and 2 were available from our previous work.[9]

Methanol was carefully dried by distillation from Mg and redistilled from anhydrous $CuSO_4$.[17] The content of water was kept as low as possible to prevent side reactions. Thus, cation 1 may undergo ring opening to yield the strongly colored conjugate base of 1,5-diphenyl-2-pentene-1,5-dione, and cation 2 may undergo OH^--promoted dealkylation to 2,6-diphenyl-4-pyranone.[18]

Triethylamine was first distilled from sodium and then from α-naphthyl isocyanate until a sample of the distillate did not yield any precipitate with the isocyanate. This treatment was necessary because triethylamine contained some impurities that were very reactive toward 1 and 2. The methanol stock solution of perchloric acid (1.06×10^{-2} M) was prepared by ion exchange.[19]

Acid and base solutions in methanol were standardized by titration.

Kinetic and Equilibrium Measurements with Et_3N/Et_3NH^+ Buffers. These measurements were made in methanol buffers prepared by partial neutralization of triethylamine (pK_a = 10.88 at 25 °C in CH_3OH)[19] with perchloric acid. The methoxide ion concentrations of each buffer were calculated from the methanol autoprotolysis value (pK_w = 16.92 at 25 °C).[20] The kinetics were followed spectrophotometrically by recording the change in absorption on a Durrum 110 stopped-flow apparatus, whose mixing cell was kept at 25 °C. The buffer was obtained at time zero in the reaction cell by allowing the methanol solution of the substrate, containing a known amount of $HClO_4$, to mix with the methanol solution of the amine. The equilibrium measurements were carried out spectrophotometrically on a Beckman DB-GT apparatus. The equilibrium constants were evaluated at 25 °C from the absorbance values, taken at equilibrium, of methanol solutions initially containing the substrate (7×10^{-5} M) and the Et_3N/Et_3NH^+ buffers, yielding methoxide ion concentrations in the 10^{-6}–10^{-5} M range. The absorbance values were measured in the 320–360-nm range at 10-nm intervals. At these wavelengths the contribution to the absorbance from the 4*H*-pyran may be neglected.[21] The absorbance at each wavelength was assumed to take the form

$$A_i = \epsilon_{2,i}[2] + \epsilon_{6,i}[6]$$

The $\epsilon_{2,i}$ values were measured in the presence of perchloric acid; under these conditions the substrate did not undergo any addition. The $\epsilon_{6,i}$ values were determined in the presence of an excess of methoxide ion, so that the equilibrium was completely driven toward the adducts. Since both adducts 4 and 6 are present in equilibrium, the concentration of the latter was calculated from the [6]/[4] ratio at equilibrium (=1.1) as measured by NMR. It was implied that this ratio, involving two neutral species, should not be strongly modified by changes of ionic strength, in going from conditions of UV measurements ($[MeO^-] \simeq 10^{-6}$–10^{-5} M) to the NMR conditions ($[MeO^-] \simeq 10^{-1}$ M). From the A_i values taken at several wavelengths and in the presence of different $[Et_3N]/[Et_3NH^+]$ ratios, the concentrations of unreacted substrate and of 2*H*-pyran were calculated. It was then possible to determine the K_6 value and, therefore, the K_4 one.

NMR and electronic spectra of methanol solutions of either substrate and the buffer were identical with those observed upon addition of sodium methoxide to the substrates. Thus, triethylamine did not react appreciably with the pyrylium cations 1 and 2, at least under the relatively mild reaction conditions and the short terms of our experiments. In particular, no evidence was found that the interaction between triethylamine and the methoxy-substituted cation 2 could bring about the S_N2 demethylation of the latter to 2,6-diphenyl-4-pyranone, even in the longer times of the NMR experiments.

Kinetic experiments with benzoate/benzoic acid buffers were made by the stopped-flow method, at 20 °C, by mixing a solution containing the substrate and benzoic acid with a given fraction of an equivalent of sodium methoxide. The ionic strength was kept constant (μ = 0.01 M) with sodium bromide. The methoxide ion concentrations were calculated by using literature[22] values for the methanol autoprotolysis (pK_w = 16.86 at 20 °C) and the dissociation constant of benzoic acid in methanol (pK_a = 9.04 at 20 °C).

Determination of Rate Constants for the Formation of Adducts 4 and 6 from 2. Because of the presence of $HClO_4$ in the solution of 2, the initial concentration of the adducts is zero. After the formation of the buffer system, the reaction pattern can be described by eq 2, the contribution of the solvent as a nucleophile being neglected relative to that of MeO^-. With a buffer system, at constant methoxide ion concentration, the second-order rate constants k_4 and k_6 are replaced by the pseudo-first-order rate constants k_4' and k_6', respectively. The kinetic system is still complex, however. In order to calculate the rate constants, we have followed a classical approach[23] for the system

$$4 \underset{k_{-4}}{\overset{k_4'}{\rightleftharpoons}} 2 \underset{k_{-6}}{\overset{k_6'}{\rightleftharpoons}} 6$$

The set of differential equations for this system is given in eq 3.

$$-d[2]/dt = (k_4' + k_6')[2] - k_{-4}[4] - k_{-6}[6] \qquad (3a)$$

$$d[4]/dt = k_4'[2] - k_{-4}[4] \qquad (3b)$$

$$d[6]/dt = k_6'[2] - k_{-6}[6] \qquad (3c)$$

Integration of these equations gives eq 4, where $\lambda_2 = {}^1/_2(p + q)$,

$$[6] = [2]_0\left\{\frac{k_6'k_{-4}}{\lambda_2\lambda_3} + \frac{k_6'(\lambda_2 - k_{-4})}{\lambda_2(\lambda_3 - \lambda_2)}e^{-\lambda_2 t} + \frac{k_6'(k_{-4} - \lambda_3)}{\lambda_3(\lambda_3 - \lambda_2)}e^{-\lambda_3 t}\right\} \qquad (4a)$$

$$[4] = [2]_0\left\{\frac{k_4'k_{-6}}{\lambda_2\lambda_3} - \frac{k_4'(k_{-6} - \lambda_2)}{\lambda_2(\lambda_3 - \lambda_2)}e^{-\lambda_2 t} + \frac{k_4'(k_{-6} - \lambda_3)}{\lambda_3(\lambda_3 - \lambda_2)}e^{-\lambda_3 t}\right\} \qquad (4b)$$

$$[2] = [2]_0\left\{\frac{k_{-4}k_{-6}}{\lambda_2\lambda_3} + \frac{(\lambda_2 - k_{-4})(k_{-6} - \lambda_2)}{\lambda_2(\lambda_3 - \lambda_2)}e^{-\lambda_2 t} + \frac{(k_{-6} - \lambda_3)(k_{-4} - \lambda_3)}{\lambda_3(\lambda_3 - \lambda_2)}e^{-\lambda_3 t}\right\} \qquad (4c)$$

$\lambda_3 = {}^1/_2(p - q)$, $p = k_4' + k_{-4} + k_6' + k_{-6}$, and $q = [p^2 - 4(k_4'k_{-6} + k_6'k_{-4} + k_{-6}k_{-4})]^{1/2}$. The k_i values were obtained by putting $[4]_0 = [6]_0 = 0$ and by fitting the experimental absorbance values to those calculated from eq 4 by using a computerized method of multiparameter optimization (MINUIT).[24] As to the input of this program, we introduced the absorbance values with the corresponding times, the K_4/K_6 value as measured by NMR, ϵ_i values at the suitable wavelength, and tentative k_i values. A typical set of experimental data is reported in Table V (see Supplementary Material), together with the calculated absorbance values.

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Registry No. 1, 3558-68-7; **2**, 17539-77-4; **3**, 53856-27-2; **4**, 67069-64-1; **6**, 67069-65-2; methoxide ion, 3315-60-4.

Supplementary Material Available: Table V, experimental data for the reaction of 2 with methoxide (1 page). Ordering information is given on any current masthead page.

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