Fast Atom Bombardment Mass Spectrometry: a Useful Technique for Structural Characterization of Pyrylium, Thiopyrylium, and Pyridinium Cations

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It is shown that fast atom bombardment (f.a.b.) mass spectrometry is well suited for the study of the title compounds (thirty nine examples are given). Glycerol and bis-(2-hydroxyethyl) sulphide appear to be the best matrices. Spectra are characterized by large peaks corresponding to the intact cations. The degree of fragmentation is generally low, but significant peaks, related to the substituents on the heteroaromatic nucleus, are observed. Alkyl substituents are responsible for alkane, alkene, or alkyl losses.

Unusual fragmentation patterns, observed in the spectra of halogeno- and nitro-derivatives, are discussed in terms of bombardment-promoted solution reactions. A simple approach for accurate (3–7 p.p.m.) mass measurements, using a peak matching unit and KCl– or NaCl–glycerol solutions as the reference substance, is also presented.

The heteroaromatic pyridinium, pyrylium, and thiopyrylium ions are fundamental heterocyclic systems, and form the core of a number of natural products.[1–3] Owing to their high reactivity towards nucleophiles, such compounds are versatile intermediates for the synthesis of a number of products. Besides pyridinium ions, in recent years pyrylium and thiopyrylium cations have found valuable industrial applications, as indicated by the increasing number of patents that involve these compounds. Until now, mass spectrometry has not been used as a routine method for structural characterization of such salts: low volatility and thermal degradation are in fact limiting factors to a mass spectrometric analysis under e.i. conditions.[4,5]

In recent years the advent of a new soft ionization technique, fast atom bombardment mass spectrometry (f.a.b.–m.s.),[6] has allowed studies on polar molecules, and its application to organic salts is the natural extension. The main objective of the present work is to present f.a.b.–m.s. as the technique of choice for the determination of heteroaromatic salts, and for this purpose a large number of such compounds (**1**)—(**39**) representative of the three classes, with several different substituents, have been investigated.† The application of accurate mass measurements in f.a.b.–m.s. using mixtures of alkaline salts and glycerol as internal standards has also been exploited, in order to elucidate some unusual fragmentation patterns.

Results and Discussion

For all compounds (**1**)—(**39**), positive ion f.a.b. mass spectrometry proved to be a sensitive method of analysis. The ion at highest *m/z* value, which, in the majority of cases, is also the most abundant peak in the spectrum, refers to the naked cation. The nature of the counterion does not seem to have any effect on the spectrum.

A variety of matrices have been tried. In general the best spectra, as to ion abundances and sample lifetime, were obtained from bis-(2-hydroxyethyl) sulphide solutions. Glycerol solutions also give good spectra (cluster ions with glycerol molecules are sometimes present) while the ion signals from diacetin matrix are intense but of short duration, probably because of the solvent volatility. With 3-aminopropane-1,2-diol or tetraglyme, only a few samples give reliable spectra, this being probably due to the low solubility of the salts in these matrices. In the last solvents in fact, spectra were taken from the suspensions, rather than homogeneous solutions.

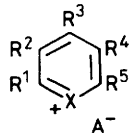
In the following discussion compounds are roughly gathered into four main groups, taking into account the substituents on the heteroaromatic ring, rather than the heteroatom; the fragmentation pattern observed always involves only the attached groups and not the aromatic nucleus.

Compounds (**1**)—(**8**).—All these compounds, characterized by the presence of phenyl substituents on the heteroatomic nucleus, give large peaks associated with the intact cation, but *no* fragment ions are observed. This could be ascribed to the well known resistance, as in the e.i. mode, to fragmentation of unfunctionalized aromatic molecules.[8]

Compounds (**9**)—(**19**).—The common feature of these compounds is the presence in the α and γ positions of alkyl groups which are responsible for the fragment ions registered in the spectrum. A representative spectrum, of 4-(1,1-diethylpropyl)-2,6-di-t-butylpyrylium tetrafluoroborate (**14**), is shown in Figure 1. The intact cation (C^+) at *m/z* 291 is the base peak in the spectrum and carries a large percentage of the total ion current. Fragment ions are present at *m/z* 276 ($C^+ - 15$), 275 ($C^+ - 16$), 263 ($C^+ - 28$), 247 ($C^+ - 44$), and 207 ($C^+ - 84$). Similar fragments, ($C^+ - 15$, $- 16$, $- 30$, and $- 56$; abundances ranging from 2—10% of the base peak) are also present in the spectra of the other compounds of this series, with the exception of (**19**), which does not fragment at all.

In order to establish the nature of these ions, we have applied a simple method (see the Experimental section) for accurate (3—7 p.p.m.) mass measurements at a resolution of 10 000 (10% valley) using a peak matching unit. 5% Potassium chloride– or sodium chloride–glycerol solution was used as the reference and the f.a.b. matrix. The exact masses thus obtained allowed us to establish that all fragment ions derive from cleavage and hydrogen rearrangements of the ring substituents with loss of alkane (CH_4, C_2H_6, C_3H_8), alkyl ($^{\bullet}CH_3$), and alkene (C_2H_4, C_4H_8, C_6H_{12}) neutral molecules. In some cases cluster ions of the type $[C_2 - H]^+$, $[C_2 + \text{anion}]^+$, $[C_3 + \text{anion}_2]^+$ are also present with abundances in the range 0.1—10% of the base

† Recently, some pyrylium and pyridinium salts have been examined by laser desorption (L.D.) and secondary ion mass spectrometry (s.i.m.s.); two compounds have also been tested by f.a.b.[7]



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(3) $R^1 = R^5 = Ph$; $R^2 = R^3 = R^4 = H$; X = NMe; A = I
(4) $R^1 = R^2 = R^4 = H$; $R^3 = R^5 = Ph$; X = O; A = ClO_4
(5) $R^1 = R^2 = R^4 = H$; $R^3 = R^5 = Ph$; X = S; A = ClO_4
(6) $R^1 = R^3 = R^5 = Ph$; $R^2 = R^4 = H$; X = O; A = ClO_4
(7) $R^1 = R^3 = R^5 = Ph$; $R^2 = R^4 = H$; X = S; A = ClO_4
(8) $R^1 = R^2 = R^4 = R^5 = Ph$; $R^3 = H$; X = O; A = BF_4
(9) $R^1 = R^5 = Bu^t$; $R^2 = R^3 = R^4 = H$; X = O; A = BF_4
(10) $R^1 = R^5 = Bu^t$; $R^2 = R^3 = R^4 = H$; X = S; A = ClO_4
(11) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = Me$; X = O; A = BF_4
(12) $R^1 = R^3 = R^5 = Bu^t$; $R^2 = R^4 = H$; X = O; A = ClO_4
(13) $R^1 = R^3 = R^5 = Bu^t$; $R^2 = R^4 = H$; X = S; A = ClO_4
(14) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = CEt_3$; X = O; A = BF_4
(15) $R^1 = R^5 = Ph$; $R^2 = R^4 = H$; $R^3 = Bu^t$; X = O; A = ClO_4
(16) $R^1 = R^5 = Ph$; $R^2 = R^4 = H$; $R^3 = Bu^t$; X = S; A = ClO_4
(17) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = Ph$; X = O; A = CF_3SO_3
(18) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = Ph$; X = S; A = ClO_4
(19) $R^1 = R^5 = Ph$; $R^2 = R^4 = H$; $R^3 = Me$; X = S; A = ClO_4
(20) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = p\text{-}MeC_6H_4$; X = O; A = ClO_4
(21) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = p\text{-}MeC_6H_4$; X = S; A = ClO_4
(22) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = p\text{-}MeOC_6H_4$; X = O; A = ClO_4
(23) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = p\text{-}MeOC_6H_4$; X = S; A = ClO_4
(24) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = p\text{-}(Me)_2NC_6H_4$; X = O; A = BF_4
(25) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = p\text{-}O_2NC_6H_4$; X = O; A = CF_3SO_3
(26) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = p\text{-}O_2NC_6H_4$; X = S; A = ClO_4
(27) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = p\text{-}ClC_6H_4$; X = O; A = ClO_4
(28) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = p\text{-}ClC_6H_4$; X = S; A = ClO_4
(29) $R^1 = R^5 = Bu^t$; $R^2 = R^4 = H$; $R^3 = m\text{-}ClC_6H_4$; X = S; A = ClO_4
(30) $R^1 = R^5 = p\text{-}ClC_6H_4$; $R^2 = R^3 = R^4 = H$; X = O; A = BF_4
(31) $R^1 = R^5 = p\text{-}BrC_6H_4$; $R^2 = R^3 = R^4 = H$; X = O; A = BF_4
(32) $R^1 = R^5 = p\text{-}BrC_6H_4$; $R^2 = R^3 = R^4 = H$; X = S; A = ClO_4
(33) $R^1 = R^2 = R^4 = H$; $R^3 = R^5 = Ph$; X = $p\text{-}ClC_6H_4N$; A = BF_4
(34) $R^1 = R^3 = Ph$; $R^2 = R^4 = H$; $R^5 = CO_2Et$; X = O; A = BF_4
(35) $R^1 = R^5 = Ph$; $R^2 = R^4 = H$; $R^3 = (Et)_2N$; X = O; A = ClO_4
(36) $R^1 = R^5 = Ph$; $R^2 = R^4 = H$; $R^3 = OMe$; X = O; A = ClO_4
(37) $R^1 = R^5 = Ph$; $R^2 = R^4 = H$; $R^3 = OCD_3$; X = O; A = ClO_4
(38) $R^1 = R^5 = Ph$; $R^2 = R^4 = H$; $R^3 = OMe$; X = S; A = ClO_4
(39) $R^1 = R^5 = Ph$; $R^2 = R^4 = H$; $R^3 = OMe$; X = MeN; A = ClO_4

peak, while clusters with the matrix were never revealed. Using bis-(2-hydroxyethyl) sulphide as the matrix, some metastable peaks were detected, related to the above fragmentations.

Compounds (**20**)—(**33**).—All the salts of this series carry a substituted phenyl ring attached to the heteroaromatic nucleus. t-Butyl groups are sometimes present and promote the same fragmentations already discussed ($C^+ - 15$, -16, -30, and -56); in particular, ions of this family are the only ones present in the spectra of compounds (**20**)—(**23**).

The f.a.b. spectrum of the pyrylium salt (**24**) contains the intact cation at *m/z* 312. Interestingly, a large fragment ion [relative abundance (r.a.) 46% of the base peak] is present at *m/z* 298 generated by loss of methylene. Loss of methylene is an extremely unusual process which in this case could be ascribed

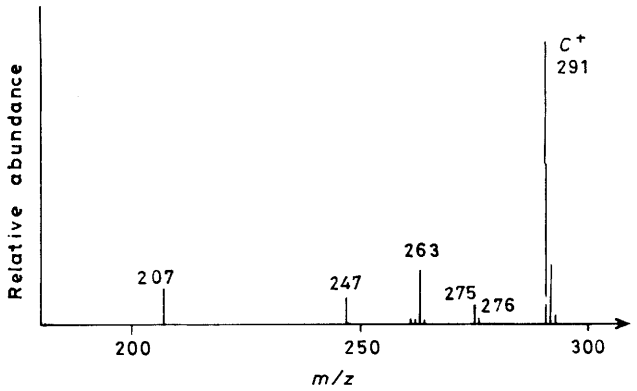

Figure 1. Positive ion f.a.b. spectrum of 4-(1,1-diethylpropyl)-2,6-di-t-butylpyrylium tetrafluoroborate (**14**) in glycerol

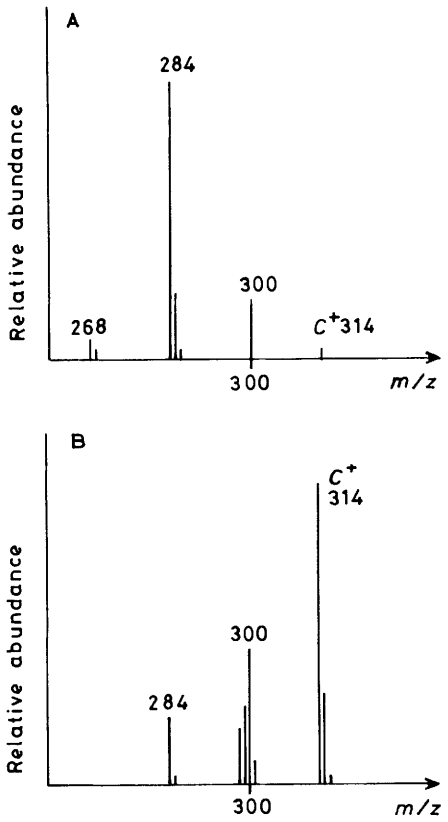

Figure 2. Positive ion f.a.b. spectrum of 4-(*p*-nitrophenyl)-2,6-di-t-butylpyrylium trifluoromethanesulphonate (**25**) in glycerol (A) and bis-(2-hydroxyethyl) sulphide (B)

to an impact-induced chemical reaction within the liquid phase,[9] directly involving the N–CH_3 bond. It is worth pointing out that the purity of compound (**24**) had been checked by n.m.r. spectroscopy and elemental analysis, in order to exclude the presence of homologous impurities.

The f.a.b. spectrum of the pyrylium derivative (**25**) was first recorded from a solution of glycerol and then from a solution of bis-(2-hydroxyethyl) sulphide. Both spectra are reported in Figure 2. In glycerol, the dominant fragment ion is 30 mass units lower than the cation and is clearly generated by a glycerol-promoted reduction of the nitro group to an amino group. Partial reduction of the nitro compound to *N*-arylhydroxylamine produces a fragment ion at *m/z* 300. This spectrum is one of the two (for the other *vide infra*) where the base peak is not

associated to the intact cation. However, a more conventional spectrum was obtained when glycerol was replaced by bis-(2-hydroxyethyl) sulphide. In this case, the ion signal generated by the cation is the base peak, again the peak at *m/z* 300 is fairly large (44% relative abundance), while the peak derived from complete reduction of the nitro group is not particularly large (25% r.a.). A similar situation is observed in the spectrum recorded from tetraglyme.

The reduction process generated by the matrix seems to be promoted by the high-energy ion beam typical of f.a.b. When in fact the bis-(2-hydroxyethyl) sulphide solution of (**25**) was left under high flux bombardment (neutral Xe atoms obtained by charge exchange of 6 keV, 30 μA Xe^+ ions) for 10 min or more, the initial ratio *m/z* $314^+/284^+$ of 4/1 changed to a plateau value of 1/6. However, the ratio *m/z* $314^+/284^+$ of 1/12 did not change significantly when using glycerol, whose reducing power is immediately implicated in the short bombardment time necessary to register the spectrum. The behaviour of the thiopyrylium salt (**26**) exactly parallels that of the pyrylium analogue (**25**).

Compounds (**27**)—(**33**) are all characterized by the presence of chlorine or bromine on the phenyl substituents of the heteroaromatic nucleus. The spectra of all these compounds show, without exception, peaks arising from a dehalogenation process with addition of H (confirmed by high resolution measurements), namely *m/z* $[C^+ - 35\ (37) + 1]$ for chlorinated compounds and $[C^+ - 79\ (81) + 1]$ for brominated ones. The relative abundance of these peaks, with respect to C^+ (base peak of the spectrum) is 20—30% in glycerol, without evident relation to the number and type of the halogen atoms present in the ion. The only exception is the pyridinium salt (**33**) where dehalogenation appears to be limited (4% r.a. of the corresponding peak).

These peaks are less abundant using solutions of bis-(2-hydroxyethyl) sulphide and more prominent in tetraglyme. The general feature of this dehalogenation reaction is that it does not appreciably fluctuate over the period of irradiation.

The dehalogenation reaction in f.a.b.–m.s. is not an unknown process[9,10] and has been already discussed by McCloskey.[11] We suggest that these high-energy processes should be considered as surface reactions occurring in close proximity to the particle impact. The energy transfer in that portion of the sample is also sufficient to promote sputtering, this being the reason why the dehalogenated ions do not accumulate during irradiation.

It is worth pointing out that the reduction of the nitro group to an amino group in compounds (**25**) and (**26**) could represent a low-energy process compared to the dehalogenation one. Thus, this reaction could also occur in regions where the desorption phenomenon is limited. It follows that in this case the reduction product undergoes accumulation during f.a.b.

These speculations are consistent with the observed spectra of the halogeno and nitro derivatives and also with the formation of oxidized compounds such as glyceraldehyde derived from glycerol under fast atom bombardment.[12]

Compounds (**34**)—(**39**).—As to the salt (**34**) no fragment ions were observed. The spectrum of (**35**) shows two peaks (r.a. 4 and 3% respectively) 30 and 44 a.m.u. lower than the mass of the intact cation, formally related to losses of ethane and propane.

The spectra of compounds (**36**), (**38**), and (**39**) all show $(C^+ - 14)$ ions; this peak is particularly large (*m/z* 249; 12 times more abundant than C^+) in the spectrum of the pyrylium salt taken in glycerol (Figure 3), but has comparable intensity to C^+ in bis-(2-hydroxyethyl) sulphide and tetraglyme. The thiopyrylium salt shows a fairly large $(C^+ - 14)$ peak (r.a. 68% in glycerol) whilst the corresponding peak in the pyridinium salt is only 6% of the intact cation.

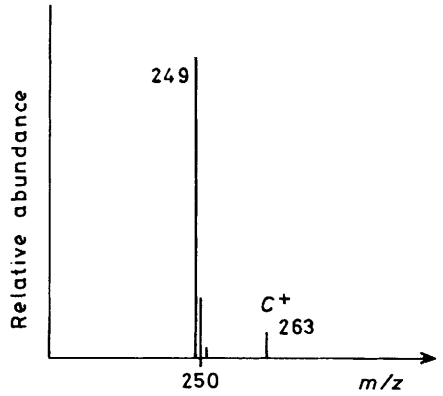

Figure 3. Positive ion f.a.b. spectrum of 4-methoxy-2,6-diphenylpyrylium perchlorate (**36**) in glycerol

These peaks could be formed by impact-induced displacement of the 4-methoxy group before desorption, to yield the 4-hydroxy derivative. The transformation of a methoxy group into a hydroxy group has already been observed during f.a.b. exposure of a 6-methoxypurine derivative[9] Nevertheless, fragmentation with hydrogen rearrangement could be an alternative. In order to check these hypotheses we submitted the deuteriated pyrylium salt (**37**) to f.a.b. analysis. Also in this case the largest peak in the spectrum occurs at *m/z* 249 with no evidence of deuterium incorporation in the fragment ion, this being indicative in favour of the former suggestion. Accordingly, since the nucleophilic displacement of the 4-methoxy group in heteroaromatic cations is a well known reaction,[13] we suggest that in our case the reaction could be promoted, during f.a.b. exposure, by traces of water absorbed by the matrix during the sample preparation.

Conclusions

F.a.b. appears to be a very useful analytical tool in the analysis of the heteroaromatic pyrylium, thiopyrylium, and pyridinium salts. All the compounds examined gave large peaks corresponding to the intact cations; unusual fragment ions, generally different from those expected from gas phase decomposition, are sometimes present and could aid structural identification. However, the existence of a fragmention pattern is not always readily predictable.

Glycerol, as the matrix commonly used, generally gives good results. Bis-(2-hydroxyethyl) sulphide moderates the overall energy and reduces the amount of fragmention observed.

Experimental

Solvents for f.a.b. mass measurements were Fluka analytical grade, water free, products. Glycerol was distilled before use. Sodium chloride– and potassium chloride–glycerol solutions (5% w/v), used as a reference for high-resolution measurements, were prepared by stirring the salt in glycerol for 3 h.

Mass spectra were run on a Kratos MS 80 instrument, equipped with post-acceleration detector and high-field magnet, using a Xenon beam of 6 keV energy and current of *ca.* 3×10^{-5} A. Spectra were routinely recorded at resolution 1 000 from *ca.* 5 μg samples dissolved in the matrix (3 μl). High-resolution experiments were performed at resolution 10 000 (10% valley) using a peak-matching unit. Unknown peaks were referred to the clusters of glycerol with itself and with sodium or potassium ions.

^1H N.m.r. spectra were recorded with a Bruker WP 80 SY

spectrometer and chemical shifts are quoted in p.p.m. relative to internal Me_4Si.

The following salts were prepared according to literature methods. 2,6-Diphenylpyrylium perchlorate (**1**);[14] 2,6-diphenylthiopyrylium perchlorate (**2**);[15] *N*-methyl-2,6-diphenylpyridinium iodide (**3**);[16] 2,4-diphenylpyrylium perchlorate (**4**);[17] 2,4-diphenylthiopyrylium perchlorate (**5**);[18] 2,4,6-triphenylpyrylium perchlorate (**6**);[19] 2,4,6-triphenylthiopyrylium perchlorate (**7**);[20] 2,3,5,6-tetraphenylpyrylium tetrafluoroborate (**8**);[21] 2,6-di-t-butylpyrylium tetrafluoroborate (**9**);[14] 2,6-di-t-butylthiopyrylium perchlorate (**10**);[15] 4-methyl-2,6-di-t-butylpyrylium tetrafluoroborate (**11**);[22] 2,4,6-tri-t-butylpyrylium perchlorate (**12**);[23] 2,4,6-tri-t-butylthiopyrylium perchlorate (**13**);[24] 4-(1,1-diethylpropyl)-2,6-di-t-butylpyrylium tetrafluoroborate (**14**);[25] 2,6-diphenyl-4-t-butylpyrylium perchlorate (**15**);[26] 4-phenyl-2,6-di-t-butylpyrylium trifluoromethanesulphonate (**17**);[27] 4-phenyl-2,6-di-t-butylthiopyrylium perchlorate (**18**);[24] 4-methyl-2,6-diphenylthiopyrylium perchlorate (**19**);[28] 2,6-di-t-butyl-4-(*p*-tolyl)thiopyrylium perchlorate (**21**);[24] 4-*p*-methoxyphenyl-2,6-di-t-butylthiopyrylium perchlorate (**23**);[24] 4-(*p*-nitrophenyl)-2,6-di-t-butylthiopyrylium perchlorate (**26**);[29] 4-(*p*-chlorophenyl-2,6-di-t-butylthiopyrylium perchlorate (**28**);[24] 4-(*m*-chlorophenyl)-2,6-di-t-butylthiopyrylium perchlorate (**29**);[29] 2,6-di-(*p*-chlorophenyl)pyrylium tetrafluoroborate (**30**);[30] 2,6-di-(*p*-bromophenyl)pyrylium tetrafluoroborate (**31**);[30] 2,6-di-(*p*-bromophenyl)thiopyrylium perchlorate (**32**);[15] *N*-(*p*-chlorophenyl)-2,4-diphenylpyridinium tetrafluoroborate (**33**);[31] 2-ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (**34**);[31] 4-diethylamino-2,6-diphenylpyrylium perchlorate (**35**);[32] 4-methoxy-2,6-diphenylpyrylium perchlorate (**36**);[33] 4-methoxy-2,6-diphenylthiopyrylium perchlorate (**38**);[34] and *N*-methyl-2,6-diphenyl-4-methoxypyridinium perchlorate (**39**).[13b]

2,6-*Diphenyl*-4-t-*butylthiopyrylium Perchlorate* (**16**).—This was obtained by treating compound (**15**) with sodium sulphide in aqueous acetone as described for the preparation of (**7**).[20] Owing to the presence of a trace amount of unchanged (**15**), the product mixture was treated with further sodium sulphide to afford the pure thiopyrylium salt (**16**) (42% overall), $\delta_H(CD_3OD)$ 1.65 (9 H, s, 4-Bu^t), 7.6—8.2 (10 H, m, 2- and 6-Ph), and 8.94 (2 H, s, 3- and 5-H); 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%).

2,6-*Di-t-butyl*-4-(p-*tolyl*)*pyrylium* (**20**), 4-(p-*Methoxyphenyl*)-2,6-*di-t-butylpyrylium* (**22**), *and* 4-(p-*Chlorophenyl*)-2,6-*di-t-butylpyrylium* (**27**) *Perchlorates*.—These were prepared from the corresponding pentane-1,5-diones,[24] according to the procedure previously described for the preparation of compound (**29**).[29]

Compound (**20**): (90%), $\delta_H(CD_3OD)$ 1.59 (18 H, s, 2- and 6-Bu^t), 2.51 (3 H, s, Me), 7.54 (2 H, A_2B_2 system, *J* 8.6 Hz, 3′- and 5′-H), 8.19 (2 H, A_2B_2 system, *J* 8.6 Hz, 2′- and 6′-H), and 8.27 (2 H, s, 3- and 5-H); m.p. 244—245 °C (Found: C, 62.8; H, 7.1. $C_{20}H_{27}ClO_5$ requires C, 62.7; H, 7.1%).

Compound (**22**): (92%), $\delta_H(CD_3OD)$ 1.58 (18 H, s, 2- and 6-Bu^t), 3.98 (3 H, s, OMe), 7.26 (2 H, A_2B_2 system, *J* 9.1 Hz, 3′- and 5′-H), 8.18 (2 H, s, 3- and 5-H), and 8.35 (2 H, A_2B_2 system, *J* 9.1 Hz, 2′- and 6′-H); m.p. 231—232 °C (Found: C, 60.0; H, 6.8. $C_{20}H_{27}ClO_6$ requires C, 60.2; H, 6.8%).

Compound (**27**): (93%), $\delta_H(CD_3OD)$ 1.60 (18 H, s, 2- and 6-Bu^t), 7.73 (2 H, A_2B_2 system, *J* 9.0 Hz, 3′-and 5′-H), 8.23 (2 H, A_2B_2 system, *J* 9.0 Hz, 2′- and 6′-H), and 8.31 (2 H, s, 3- and 5-H); m.p. 253—255 °C (Found: C, 56.5; H, 6.0. $C_{19}H_{24}Cl_2O_5$ requires C, 56.6; H, 6.0%).

4-(p-*Dimethylaminophenyl*)-2,6-*di-t-butylpyrylium Tetrafluoroborate* (**24**).—The salt (**9**) (1.4 g, 5 mmol), *N*,*N*-dimethylaniline (0.65 g, 5.4 mmol), anhydrous sodium acetate (0.44 g, 5.4 mmol), and acetic acid (50 ml) were refluxed together for 2 h. The volume was reduced to *ca.* 10 ml by partial distillation of the solvent. Carbon tetrachloride (200 ml) was then added and the mixture was left at 0 °C for 1 h. The precipitate was collected by filtration and dissolved in the minimum amount of CH_2Cl_2. The residue (sodium salts) was removed by filtration and diethyl ether–light petroleum (b.p. 40—70 °C) (1:1 v/v) was added to the solution until complete precipitation of the product (**24**) (19%) had occurred; $\delta_H(CD_3OD)$ 1.50 (18 H, s, 2- and 6-Bu^t), 3.27 (6 H, s, NMe_2), 6.99 (2 H, A_2B_2 system, *J* 9.4 Hz, 3′- and 5′-H), 7.81 (2 H, s, 3- and 5-H), and 8.24 (2 H, A_2B_2 system, *J* 9.4 Hz, 2′- and 6′-H); m.p. 180—182 °C (Found: C, 63.0; H, 7.7; N, 3.5. $C_{21}H_{30}BF_4NO$ requires C, 63.2; H, 7.6; N, 3.5%).

4-(p-*Nitrophenyl*)-2,6-*di-t-butylpyrylium Trifluoromethanesulphonate* (**25**).—This was prepared by condensing *p*-nitrostyryl t-butyl ketone and pinacolone with CF_3SO_3H, as described for the preparation of compound (**17**).[27] The crude salt was dissolved in the minimum amount of CH_2Cl_2 containing 1—2 drops of CF_3SO_3H, and precipitated with dry ether to give the pure *salt* (**25**) (47%); $\delta_H(CD_3OD)$ 1.63 (18 H, s, 2- and 6-Bu^t), 8.46 (4 H, pseudo-singlet, 2′-, 3′-, 5′-, and 6′-H), and 8.48 (2 H, s, 3-and 5-H); m.p. 278—280 °C (Found: C, 51.7; H, 5.3; N, 3.0. $C_{20}H_{24}F_3NO_6S$ requires C, 51.8; H, 5.2; N, 3.0%).

p-*Nitrostyryl t-Butyl Ketone*.—Pinacolone (10 g, 0.1 mol), *p*-nitrobenzaldehyde (15.1 g, 0.1 mol), and ethanol (95%; 100 ml) were heated with stirring until complete dissolution of the aldehyde had occurred. The reaction flask was then immersed in a water bath maintained at 45—50 °C (higher temperatures were found to give poorer yields). Aqueous NaOH (10%; 10 ml) was then added over 10 min with stirring. The stirring was continued for 30 min, when dilute HCl was added until the mixture became acidic. The solid product obtained on cooling the reaction mixture was collected and recrystallized from 95% ethanol (yield 74%), m.p. 127—128 °C.

2,6-*Diphenyl*-4-[$^2H_3$]*methoxypyrylium Perchlorate* (**37**).—This was obtained by recrystallization of compound (**36**) from CD_3OD (Erba). The complete exchange of the methoxy group was confirmed by ^1H n.m.r. spectroscopy in CD_3CN.

Acknowledgements

Thanks are due to Professor R. Nicoletti for helpful discussions and for his critical reading of the manuscript. High-resolution mass measurements were performed by Dr. S. Ceccarelli. We thank the Servizio di Microanilisi, Area della Ricerca di Roma del CNR, for elemental analyses. Work supported in part by Ministero della Pubblica Istruzione

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Received 2nd *April* 1986; *Paper* 6/653