

## ***N*-Oxides and Related Compounds. Part 58.<sup>1</sup> Some Precursors of Pyridinium Methylide**

By Jayant B. Bapat, Jan Epszajn, Alan R. Katritzky,\* and Bernard Plau, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

1-*t*-Butoxycarbonylmethylpyridinium ion (3) is pyrolysed to yield successively the 1-carboxymethyl- and the 1-methyl-pyridinium ions. The intermediate ylide (1) could be trapped by benzaldehyde and other electrophiles.

1-Carboxymethylpyridinium betaine (5) reacts with aldehydes as the ylide tautomer (6) to give products (8) of aldol reactions, transformations of which are described. The reactions of various other electrophiles with the betaine (5) have been investigated.

The ylide (20) from the cation (3) reacts as expected with methyl iodide, benzyl bromide, and benzoyl chloride (at 0 °C). At 25 °C, benzoyl chloride gives a product of further acylation, as do other acid halides.

PYRIDINIUM ylides have received considerable attention in recent years as synthetic intermediates. In particular, many of these ylides stabilized by an electron-withdrawing group attached to the methylene carbon have been isolated. When this is a carbonyl group the ylides have been called 'enol betaines,' and these have been investigated extensively by German workers.<sup>2-4</sup>

In contrast, reports on the simple pyridinium methylides [*cf.* (1)], which are not stable enough for isolation, have been scarce. Kröhnke<sup>2</sup> reported the piperidine-catalysed condensation of 1-methylpyridinium bromide with benzaldehyde to give the corresponding alcohol in 80% yield, *via* the ylide (1). Recently several papers have appeared on deuterium-exchange studies of

<sup>1</sup> Part 57, A. S. Afridi, A. R. Katritzky, and C. A. Ramsden, *J.C.S. Perkin I*, 1977, 1436.

<sup>2</sup> F. Kröhnke, *Angew. Chem.*, 1953, **65**, 605.

<sup>3</sup> F. Kröhnke and W. Zecher, *Angew. Chem. Internat. Edn.*, 1962, **1**, 626.

<sup>4</sup> F. Kröhnke, *Angew. Chem. Internat. Edn.*, 1963, **2**, 225.

pyridinium salts,<sup>5-7</sup> and Ratts *et al.*<sup>8,9</sup> have trapped and studied the ylide (1) and its isomer (2) by decarboxylative methods.

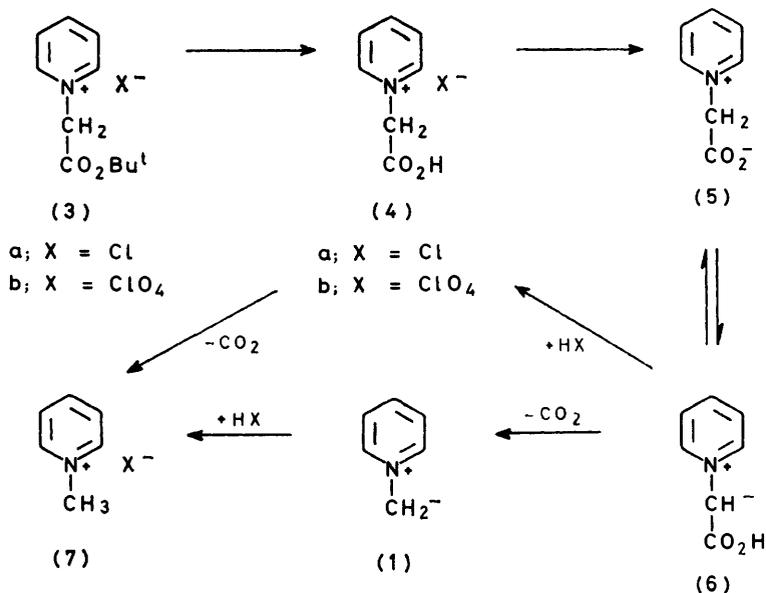


We have been interested in extending the synthetic potential of pyridinium ylides, and in particular in the preparation of stable precursors of pyridinium methylide (1) and the mechanistic study of its reactions. This paper describes the preparation and some reactions of

180 °C the ester (3b) and the acid (4b) both evolved carbon dioxide to give the salt (7) in 40% yield; there was considerable decomposition, but we proceeded with experiments designed to trap the ylides (1) and (6).

The tautomerism of the betaine (5) with the carboxylide (6), and the possible decarboxylation of (6) to form the simple ylide (1) were realised by Ratts *et al.*,<sup>9</sup> who prepared a series of 1-(β-aryl-β-hydroxyethyl)pyridinium salts (9) by the reactions of bromoacetic acid and pyridine with aromatic aldehydes. These workers could not distinguish conclusively between routes (5) → (6) → (8) → (9) and (5) → (1) → (10) → (9), but favoured the latter.

We now find that the free betaine (5) (isolated from the chloride by ion-exchange) reacts with aromatic



SCHEME 1

1-t-butoxycarbonylmethylpyridinium salts [general formula (3)] and the betaine (5) of the corresponding free acid (4).

Although 1-n-butoxycarbonylmethylpyridinium salts have been reported,<sup>10</sup> to our knowledge those of the corresponding t-butyl ester were not known. We have prepared the hygroscopic chloride salt (3a) in 50% yield by quaternisation of pyridine with t-butyl chloroacetate.<sup>11</sup> The perchlorate (3b) was a stable compound, m.p. 96–97 °C. The pyrolytic conversion of the t-butyl ester (3a) into the N-methyl salt (7) occurred in stages (Scheme 1). Heating the ester salt (3a) (m.p. 96–97 °C) at 140 °C led only to the loss of isobutene, and the acid salt (4a) was isolated in good yield, and characterised by its i.r. and n.m.r. spectra and direct synthesis from pyridine and chloroacetic acid. At

aldehydes to give the addition products (8). They are unstable and were characterised as the bromides (11). Our reaction thus certainly occurs by way of the tautomer (6) and not (1): it is also probable that, under the conditions previously employed,<sup>9</sup> route (5) → (6) → (8) → (9) is followed. Our u.v. spectral comparisons of the betaine (5)  $\rightleftharpoons$  (6) ( $\lambda_{\text{max}}$  262 nm,  $\epsilon$  4 800) and the hydrochloride ( $\lambda_{\text{max}}$  261 nm,  $\epsilon$  5 000) show that the betaine predominates greatly in solution.

*Reactions of the Betaine (5).*—The aldol reaction with the betaine (5) apparently yields only one of the two possible stereoisomers of (8). The n.m.r. coupling constants of ca. 4 Hz between the two aliphatic CH systems indicate a *gauche* relation. If we make the reasonable assumption that the large pyridinio- and aryl groups will be mutually *trans*, this indicates stereostructure (13) for these products. Heating the aldol product (11c) in nitrobenzene [solvent used<sup>9</sup> for the

<sup>5</sup> J. A. Zoltewicz and R. E. Cross, *J.C.S. Perkin II*, 1974, 1363.

<sup>6</sup> J. A. Zoltewicz and R. E. Cross, *J.C.S. Perkin II*, 1974, 1368.

<sup>7</sup> R. E. Cross, *Diss. Abs. Int. B*, 1972, **32**, 5685 (*Chem. Abs.*, 1972, **77**, 47776n).

<sup>8</sup> R. K. Howe and K. W. Ratts, *Tetrahedron Letters*, 1967, 4743; W. G. Phillips and K. W. Ratts, *ibid.*, 1969, 1383.

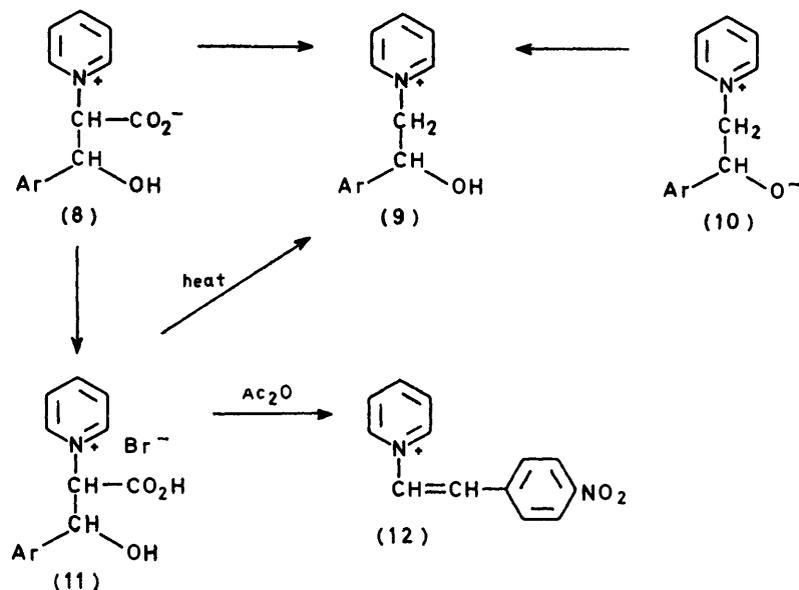
<sup>9</sup> K. W. Ratts, R. K. Howe, and W. G. Phillips, *J. Amer. Chem. Soc.*, 1969, **91**, 6115.

<sup>10</sup> N. N. Mel'nikov, N. D. Sukhareva, and O. P. Arkhipova, *Zhur. priklad. Khim.*, 1947, **20**, 642 (*Chem. Abs.*, 1949, **43**, 6 977b).

<sup>11</sup> R. H. Baker, *Org. Synth.*, Coll. Vol. III, 1955, p. 144.

one-pot preparation of (9)] gave as expected the alcohol (9; Ar = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>). The aldol product bromides were also heated in acetic anhydride, but only the

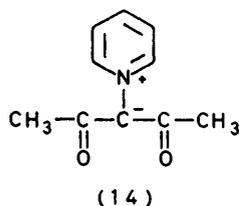
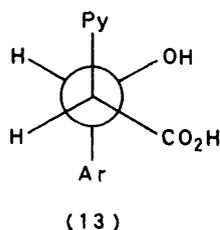
showed two different *para*-substituted aromatic patterns and two singlets (3 H each) for the methoxy-groups at  $\delta$  3.52 and 3.75.



SCHEME 2

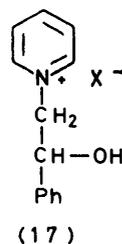
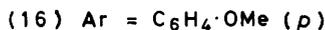
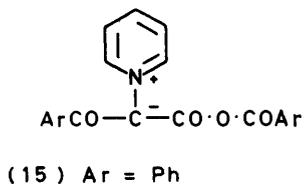
*p*-nitrophenyl derivative gave the expected vinylpyridinium salt (12).

The betaine (5) was treated with various electrophilic reagents. Acetic anhydride gave the diacetylmethylide (14), the structure of which follows from analytical and

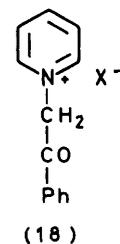


*Pyrolytic Reactions of the *t*-Butyl Esters (3).*—The high temperature required for the breakdown of the ester (3) to the ylide (1) *via* the acid (4) meant that the reactions were accompanied by considerable decomposition, which decreased the yields. Refluxing the salt (3a) in an excess of benzaldehyde gave the expected alcohol (17a) in 45% yield, whereas heating in benzoyl chloride produced a low yield of the *N*-phenacyl salt (18a) [characterised as the perchlorate (18b)]. Benzophenone similarly gave the expected alcohol (19) in 6% yield.

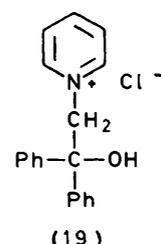
*Base-catalysed Reactions of the *t*-Butyl Esters (3).*—Generation of the ylide (20) by lithium di-isopropylamide complexed with hexamethylphosphoric triamide<sup>12</sup> in tetrahydrofuran and subsequent treatment with benzoyl chloride gave the phenacylpyridinium salt (18b)



a; X = Cl  
b; X = ClO<sub>4</sub>



a; X = Cl  
b; X = ClO<sub>4</sub>  
c; X = Br



spectral data [particularly the singlet (6 H) for two equivalent methyl groups at  $\delta$  2.35]. Alkyl bromides in ethanol or methanol gave only the hydrobromide of (5); attempted reactions with alkyl bromides in the absence of solvent gave complex mixtures of polymeric products. Benzoyl chloride and triethylamine gave the new ylide (15). To prove the structure of the ylide (15), the corresponding *para*-methoxy-ylide (16) was prepared by using anisoyl chloride. The n.m.r. spectrum

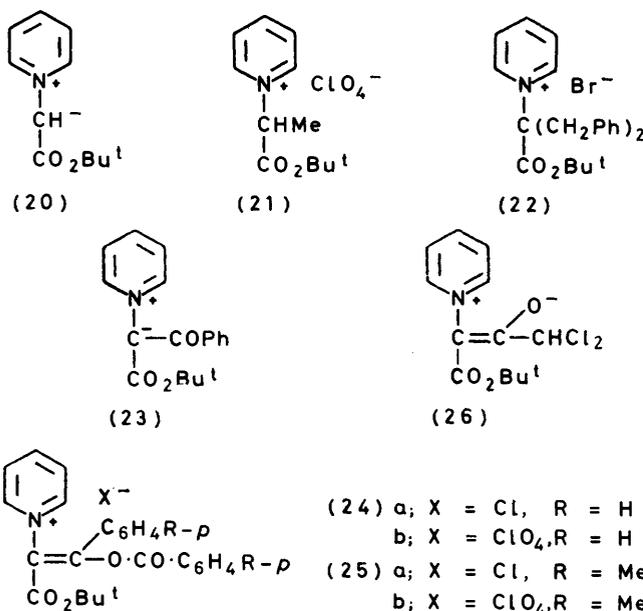
<sup>12</sup> E. M. Kaiser and G. D. Petty, *Synthesis*, 1975, 705.

in low yield: the ester group is evidently lost by hydrolysis in the work-up. Alkylations and arylations with sodium hydride in dimethylformamide were unsuccessful. These findings support the observation of Ritchie *et al.*<sup>13</sup>

<sup>13</sup> C. A. Henrick, E. Ritchie, and W. C. Taylor, *Austral. J. Chem.*, 1967, **20**, 2441, 2455, 2467.

that the choice of base and solvent is critical in such reactions.

Sodium hydride in acetonitrile was finally found to be a satisfactory base-solvent combination: precautions must be taken to exclude moisture as even traces of water greatly reduce the yields. Under these conditions, the ylide (20) was generated and successfully monoalkylated with methyl iodide and benzyl bromide to yield the expected products [*cf.* (21)]. Prolonged treatment with an excess of benzyl bromide led to the dibenzyl derivative (22).



The reaction with benzoyl chloride is temperature-dependent: at 0 °C the product was the betaine (23). However reaction at 25 °C gave the salt (24) derived from the betaine (23) by reaction with a second molecule of benzoyl chloride. The structure (24) was confirmed by analysis and spectral data and by n.m.r. spectral comparison with the *p*-methyl compound (25) prepared from toluoyl chloride. The n.m.r. spectrum of (25) showed two different *para*-substituted aromatic patterns and two singlets for the methyl protons. Pyrolysis of the salt (24b) resulted in the loss of isobutene and carbon dioxide: recrystallisation of the residue from ethanol removed one benzoyl group to leave the phenacyl salt (18b) in 50% yield. Dichloroacetyl chloride similarly gave the ylide (26).

The ease of preparation of the salts (3) and conversion into the ylide (20) suggests potential as a synthetic intermediate.

#### EXPERIMENTAL

*1-t-Butoxycarbonylmethylpyridinium Chloride (3a) and Perchlorate (3b).*—Pyridine (7.9 g, 0.1 mol) and *t*-butyl chloroacetate (15 g, 0.1 mol) (prepared<sup>11</sup> in 67% yield;

<sup>11</sup> Beilsteins Handbuch der Organischen Chemie, eds. B. Prager and P. Jacobson, Springer-Verlag, Berlin, 1935, XX, p. 226.

b.p. 85 °C at 67 mmHg) were refluxed for 12 h in absolute EtOH (60 ml). EtOH was removed at 20 mmHg, and water (20 ml) was added. The solution was extracted with Et<sub>2</sub>O (3 × 10 ml). The aqueous layer was evaporated at 20 mmHg, MeOH (50 ml) added, and after drying (Na<sub>2</sub>SO<sub>4</sub>) the solvent was removed at 20 mmHg. The residue crystallised in a desiccator (P<sub>2</sub>O<sub>5</sub>) as yellowish prisms of a hydrate (11.6 g, 50%), m.p. 88–96 °C;  $\nu_{\text{max}}$  (Nujol) 1740 (C=O) and 1640 cm<sup>-1</sup> (C=N);  $\delta$  (D<sub>2</sub>O; 60 MHz) 1.52 (9 H, s), 5.6 (2 H, s), and 8.5 (5 H, m). The crude chloride (3a) was converted with sodium perchlorate into the perchlorate (3b), which crystallised from EtOH as prisms, m.p. 96–97 °C (Found: C, 45.0; H, 5.5; N, 4.8. C<sub>11</sub>H<sub>16</sub>ClNO<sub>6</sub> requires C, 44.6; H, 5.4; N, 4.9%).

*1-Carboxymethylpyridinium Betaine (5).*—(a) Pyridine (79 g, 1 mol) and chloroacetic acid (103.9 g, 1.1 mol) were kept in EtOH (150 ml) for 5 days at 20 °C. The hemihydrochloride which separated was washed with, and crystallised from, EtOH to give thick needles (132 g, 82%), m.p. 163–165 °C (decomp.) [lit.,<sup>14</sup> 159 °C (decomp.)] (Found: C, 51.2; H, 5.0; N, 8.5. Calc. for C<sub>14</sub>H<sub>15</sub>ClN<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O: C, 51.4; H, 5.2; N, 8.5%).  $\nu_{\text{max}}$  (Nujol) 1730 cm<sup>-1</sup>;  $\delta$  (D<sub>2</sub>O) 8.85–7.9 (5 H, m) and 5.2 (2 H, s).

(b) The hemihydrochloride (32.8 g, 0.1 mol) in 15% HCl (30 ml) was evaporated at 50 °C and 10 mmHg. Crystallisation from water gave prisms of 1-carboxymethylpyridinium hydrochloride (28 g, 80.9%), m.p. 195–197 °C (decomp.) [lit.,<sup>15</sup> 202 °C (decomp.)] (Found: C, 48.1; H, 4.6; N, 8.2. Calc. for C<sub>7</sub>H<sub>8</sub>ClNO<sub>2</sub>: C, 48.6; H, 4.6; N, 8.1%).  $\nu_{\text{max}}$  (Nujol) 3390 and 1730 cm<sup>-1</sup>;  $\lambda_{\text{max}}$  (H<sub>2</sub>O) 227 ( $\epsilon$  4 000) and 261 nm (5 000);  $\delta$  (D<sub>2</sub>O) 8.9–7.95 (5 H, m) and 5.26 (2 H, s).

(c) The hemihydrochloride (65.6 g, 0.2 mol) in distilled water (500 ml) was passed through an Amberlite IRA-400 column (500 g), followed by water (1 l). The combined eluates were evaporated at 40–50 °C and 15 mmHg and EtOH (150 ml) was added. The solid crystallised from MeOH as prisms of the betaine (5) (23.8 g, 87%), m.p. 154–156 °C (decomp.) [lit.,<sup>14</sup> 150 °C (decomp.)] (Found: C, 60.9; H, 5.1; N, 10.2. Calc. for C<sub>7</sub>H<sub>7</sub>NO<sub>2</sub>: C, 61.3; H, 5.1; N, 10.2%).  $\nu_{\text{max}}$  (Nujol) 3460, 1665, and 1635 cm<sup>-1</sup>;  $\lambda_{\text{max}}$  (H<sub>2</sub>O) 229 ( $\epsilon$  3 600) and 261 nm (4 800);  $\delta$  (D<sub>2</sub>O) 8.95–8.05 (5 H, m) and 5.5 (2 H, s).

*Reactions of the Betaine (5) with Aromatic Aldehydes.*—Compound (5) (1.37 g, 0.01 mol) and the aldehyde (0.025 mol) were heated under reflux in EtOH (35 ml) for 2 h. Products were filtered off and washed with EtOH and Me<sub>2</sub>CO. The aldol products were suspended in water and an excess of aqueous HBr was added. The solutions were evaporated at 50 °C and 15 mmHg and the resulting solids crystallised from EtOH (see Table).

*Decarboxylation of Compound (11c).*—Compound (11c) (0.92 g, 0.0025 mol) in nitrobenzene (10 ml) was heated at 135 °C for 1 h. The solid product crystallised from EtOH as needles of 1-( $\beta$ -hydroxy- $\beta$ -*p*-nitrophenylethyl)pyridinium bromide (9) (0.6 g, 74%), m.p. 278–280 °C (decomp.) [lit.,<sup>9</sup> 275–276 °C (decomp.)] (Found: C, 48.1; H, 4.2; N, 8.8. Calc. for C<sub>13</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>3</sub>: C, 48.0; H, 4.0; N, 8.6%).  $\nu_{\text{max}}$  (Nujol) 3260 cm<sup>-1</sup>;  $\delta$  (CF<sub>3</sub>·CO<sub>2</sub>H) 9.0–7.6 (9 H, m), 5.12 (1 H), and 4.93 (2 H, m).

*Reaction of Compound (11c) with Acetic Anhydride.*—Compound (11c) (1.84 g, 0.005 mol) in Ac<sub>2</sub>O (20 ml) was heated at 80 °C for 3 h. Excess of Ac<sub>2</sub>O was evaporated off at 50 °C at 15 mmHg; the residue crystallised from

<sup>15</sup> F. Kröhnke and K. Gerlach, *Chem. Ber.*, 1962, **95**, 1108.

EtOH as yellow needles of 1-(*p*-nitrostyryl)pyridinium bromide (12) (0.92 g, 60%), m.p. 280—282 °C (Found: C, 51.1; H, 3.5; N, 8.9.  $C_{13}H_{11}BrN_2O_2$  requires C, 50.8; H, 3.6; N, 9.1%);  $\nu_{\max}$  (Nujol) 1 625, 1 605, and 1 595  $cm^{-1}$ ;  $\delta$  ( $CF_3 \cdot CO_2H$ ) 9.2—7.5 (m).

**Reaction of the Betaine (5) with Benzoyl Chloride and Triethylamine.**—The solid betaine (5) (2.74 g, 0.04 mol) was added to the freshly prepared mixture of benzoyl chloride (5.6 g, 0.04 mol) and  $Et_3N$  (4.25 g, 0.042 mol) in  $CHCl_3$  (50 ml). The mixture was kept for 12 h and water (200 ml) and  $CHCl_3$  (200 ml) were added. The organic layer was separated and evaporated at 50 °C and 15 mmHg. The oily residue solidified on trituration with EtOH. It crystallised from  $Me_2CO$  as yellow prisms of pyridinium  $\alpha$ -(benzoyloxycarbonyl)phenacylide (15) (2.54 g, 36.8%), m.p. 135—137 °C (decomp.) (Found: C, 73.0; H, 4.5;

hemihydrobromide (1.4 g, 78%), m.p. 168—170 °C (decomp.) [lit.,<sup>14</sup> 170 °C (decomp.)] (Found: C, 44.8; H, 4.4; N, 7.3. Calc. for  $C_{14}H_{15}BrN_2O_4 \cdot H_2O$ : C, 45.0; H, 4.5; N, 7.5%).

**1-Carboxymethylpyridinium Chloride (4a).**—The salt (3a) (0.5 g, 0.022 mol) was melted under nitrogen and kept at 140 °C for 15 min. Vigorous gas evolution was observed for about 10 min. Cooling and addition of  $Et_2O$  (20 ml) gave 1-carboxymethylpyridinium chloride (0.24 g, 65%), which crystallised from EtOH as prisms, m.p. 195—198 °C (lit.,<sup>15</sup> 202 °C) (Found: C, 48.4; H, 4.8; Cl, 20.2; N, 8.1.  $C_7H_8ClNO_2$  requires C, 48.4; H, 4.6; Cl, 20.5; N, 8.1%);  $\nu_{\max}$  ( $HCBBr_3$ ) 1 720  $cm^{-1}$  (C=O);  $\delta$  ( $CDCl_3$ ; 60 MHz) 5.9 (2 H, s) and 8.1—9 (5 H, m).

**1-Methylpyridinium Perchlorate (7; X =  $ClO_4$ ).**—The acid (4b) (0.2 g, 0.000 84 mol) was heated under nitrogen: at 176 °C gas evolution was observed and the melt turned

Physical data for 1 ( $\beta$ -aryl- $\alpha$ -carboxy- $\beta$ -hydroxyethyl)pyridinium bromides

Compound	Ar	M.p. (°C)	Cryst. form	Cryst. solvent	Yield (%)	Found (%)			Formula	Calc. (%)		
						C	H	N		C	H	N
(11a)	$C_6H_5$	172—174 (decomp.)	Needles	abs. EtOH	72	51.8	4.2	4.2	$C_{14}H_{14}BrNO_3$	51.8	4.3	4.3
(11b)	$C_6H_4Cl$ ( <i>p</i> )	180—182 (decomp.)	Needles	abs. EtOH	81	46.9	3.5	4.0	$C_{14}H_{13}BrClNO_3$	47.0	3.6	3.9
(11c)	$C_6H_4-NO_2$ ( <i>p</i> )	178—180 (decomp.)	Fine needles	EtOH	96	45.2	3.5	7.8	$C_{14}H_{13}BrN_2O_5$	45.5	3.5	7.6
	I.r. ( $\nu_{\max}$ , $cm^{-1}$ ) <sup>a</sup>					N.m.r. ( $\delta$ ) <sup>b</sup>						
(11a)	3 285, 2 820, 1 740					8.75—7.70 (5 H, m), 7.3—7.0 (5 H, m), 6.12—6.08 (1 H, d, <i>J</i> 4 Hz), 5.86—5.82 (1 H, d, <i>J</i> 4 Hz)						
(11b)	3 220, 2 860, 1 745					8.9—7.7 (5 H, m), 7.4—6.9 (4 H, dd, <i>J</i> 7.1 Hz), 6.15—6.11 (1 H, d, <i>J</i> 4 Hz), 5.95—5.91 (1 H, d, <i>J</i> 4 Hz)						
(11c)	3 180, 2 790, 1 735					8.95—7.4 (9 H, m), 6.32—6.28 (1 H, d, <i>J</i> 4 Hz), 6.23—6.19 (1 H, d, <i>J</i> 4 Hz)						

<sup>a</sup> In hexachlorobutadiene. <sup>b</sup> In  $CF_3 \cdot CO_2H$  with  $Me_4Si$  external standard.

N, 4.0.  $C_{21}H_{15}NO_4$  requires C, 73.1; H, 4.3; N, 4.1%);  $\nu_{\max}$  (Nujol) 1 725 and 1 660  $cm^{-1}$ ;  $\delta$  ( $CDCl_3$ ) 8.82—7.0 (m).

**Reaction of the Betaine (5) with Anisoyl Chloride and Triethylamine.**—The solid betaine (5) (2.74 g, 0.02 mol) was added to anisoyl chloride (7.16 g, 0.04 mol) and  $Et_3N$  (4.25 g, 0.042 mol) in  $CHCl_3$  (50 ml). The mixture was kept for 12 h and water (200 ml) and  $CHCl_3$  (200 ml) were added. After evaporation the oily residue solidified on trituration with  $Et_2O$ . The *ylide* (16) crystallised from  $Me_2CO$  as yellow prisms (5.2 g, 64.6%), m.p. 124—126 °C (decomp.) (Found: C, 68.1; H, 4.5; N, 3.7.  $C_{23}H_{19}NO_6$  requires C, 68.2; H, 4.7; N, 3.5%);  $\nu_{\max}$  (Nujol) 1 720 and 1 665  $cm^{-1}$ ;  $\delta$  ( $CDCl_3$ ) 8.8—7.6 (5 H, m), 7.55—7.45 (4 H, d, *J* 9 Hz), 6.8—6.65 (2 H, d, *J* 9 Hz), 6.68—6.58 (2 H, d, *J* 9 Hz), 3.75 (3 H, s), and 3.52 (3 H, s).

**Reaction of the Betaine (5) with Acetic Anhydride.**—The betaine (5) (2.74 g, 0.02 mol) in  $Ac_2O$  (15 ml) was heated at 90 °C for 0.5 h. Excess of  $Ac_2O$  was evaporated off at 50 °C and 15 mmHg. The semi-solid residue was washed with a little  $Me_2CO$ , and crystallised from  $Me_2CO$  to give yellow needles of pyridinium diacetylmethylide (14) (1.78 g, 49%), m.p. 185—186 °C (Found: C, 67.4; H, 6.4; N, 7.6.  $C_{10}H_{11}NO_2$  requires C, 67.8; H, 6.3; N, 7.9%);  $\delta$  ( $CDCl_3$ ) 8.45—7.6 (5 H, m) and 2.35 (6 H, s).

**Reaction of the Betaine (5) with Aliphatic Halides.**—The betaine (5) (1.37 g, 0.01 mol) and an aliphatic halide (ethyl, isopropyl, or allyl bromide) (0.04 mol) were heated under reflux in MeOH (20 ml) for 5 h. Then solvent and excess of aliphatic halide were evaporated off at 50 °C and 15 mmHg (to dryness). The solid product was washed with  $Me_2CO$  and crystallised from EtOH to give needles of the

black. It was kept at 180 °C for 30 min, cooled, and extracted with  $Me_2CO$ . Evaporation at 30 °C and 15 mmHg and recrystallisation from EtOH gave 1-methylpyridinium perchlorate (0.08 g, 50%), m.p. 133—134 °C (decomp.) (lit.,<sup>16</sup> 129—130 °C).

**1-( $\beta$ -Hydroxy- $\beta$ -phenylethyl)pyridinium Chloride (17a) and Perchlorate (17b).**—The chloride (3a) (2 g, 0.0087 mol) was refluxed in benzaldehyde (10 ml) for 3 h. On cooling, the solid product was recrystallised twice from  $MeOH-Et_2O$  to give the hydroxy-chloride (17a) (0.9 g, 45%) as prisms, m.p. 234—235 °C [lit.,<sup>17</sup> 210—212 °C (decomp.)] (Found: C, 66.0; H, 6.0; N, 6.0. Calc. for  $C_{13}H_{14}ClNO$ : C, 66.2; H, 5.9; N, 6.0%);  $\nu_{\max}$  (Nujol) 3 200 (O-H) and 1 640  $cm^{-1}$  (C=N);  $\delta$  ( $D_2O$ ; 60 MHz) 4.8 (3 H, m), 7.4 (5 H, s), and 8.0—8.7 (5 H, m).

The chloride (17a) was dissolved in water (15 ml) and sodium perchlorate (2 g) in water (5 ml) added to give the perchlorate, which crystallised from hot EtOH as prisms, m.p. 212—213 °C (lit.,<sup>17</sup> 210—212 °C) (Found: C, 52.0; H, 4.7; N, 4.8. Calc. for  $C_{13}H_{14}ClNO_4$ : C, 52.1; H, 4.7; N, 4.8%);  $\nu_{\max}$  (Nujol) 3 460 (O-H), 1 640 (C=N), and 1 100  $cm^{-1}$  (Cl-O).

**1-Phenacylpyridinium Perchlorate (18b).**—The chloride (3a) (2 g, 0.0087 mol) was refluxed for 15 min in benzoyl chloride (10 ml). Water (30 ml) was added, and the mixture extracted with  $Et_2O$  (3  $\times$  50 ml). The water layer was evaporated to 5 ml and sodium perchlorate (1 g) was added. The perchlorate (18b) precipitated; it crystallised from  $MeOH-Me_2CO$  as prisms (0.05 g, 2%), m.p. 184 °C (lit.,<sup>18</sup> 189—190 °C);  $\nu_{\max}$  (Nujol) 1 710 (C=O),

<sup>17</sup> J.-A. Gautier, *Compt. rend.*, 1934, **198**, 1430 (*Chem. Abs.*, 1934, **28**, 4 222<sup>a</sup>).

<sup>18</sup> L. C. King, *J. Amer. Chem. Soc.*, 1944, **66**, 894.

<sup>16</sup> G. A. Reynolds, R. E. Adel, and J. A. VanAllan, *J. Org. Chem.*, 1963, **28**, 2683.

1 640 (C=N), and 1 100  $\text{cm}^{-1}$  (Cl-O);  $\delta$  [ $(\text{CD}_3)_2\text{CO}$ ; 60 MHz] 6.7 (2 H, s) and 8.5 (10 H, m).

Alternatively the chloride (3a) (5 g, 0.022 mol) in  $\text{HCONMe}_2$  (5 ml) was added dropwise over 5 min at 0 °C to lithium di-isopropylamide (0.022 mol) complexed by hexamethylphosphoric triamide as described in ref. 12 in  $[\text{CH}_2]_4\text{O}$  (20 ml).  $\text{HCONMe}_2$  and  $[\text{CH}_2]_4\text{O}$  had been distilled over molecular sieves and the whole reaction was performed under dry nitrogen. The heterogeneous mixture was stirred for 1 h at 0 °C, benzoyl chloride (2.9 g, 0.021 mol) was added, and the mixture was kept for 12 h at room temperature.  $[\text{CH}_2]_4\text{O}$  was removed at 50 °C and 20 mmHg and 0.025M-HCl (50 ml) added, followed by sodium perchlorate (1 g) to give the solid which crystallised from MeOH as prisms of (18b) (0.66 g, 10%).

1-( $\beta$ -Hydroxy- $\beta$ -diphenylethyl)pyridinium Chloride (19).—The chloride (3a) (2 g, 0.0087 mol) and benzophenone (10 g, 0.055 mol) were heated at 190 °C for 10 min. The cold residue was dissolved in water (15 ml) and extracted with  $\text{Et}_2\text{O}$  (3  $\times$  20 ml). The aqueous layer was evaporated at 20 mmHg to give the  $\beta$ -hydroxy-chloride, which was recrystallised twice from MeOH to give prisms (0.15 g, 6%), m.p. 249–250 °C (Found: C, 72.9; H, 5.9; Cl, 11.2; N, 4.3.  $\text{C}_{19}\text{H}_{18}\text{ClNO}$  requires C, 73.2; H, 5.8; Cl, 11.4; N, 4.5%).  $\nu_{\text{max}}$  (Nujol) 1 640  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{D}_2\text{O}$ ; 60 MHz) 5.4 (2 H, s), 7.3 (10 H, s), and 8.0 (5 H, m).

1-( $\alpha$ -*t*-Butoxycarbonylethyl)pyridinium Perchlorate (21).—Sodium hydride (0.42 g, 0.017 mol) was added at 0 °C to the salt (3a) (2 g, 0.0087 mol) in MeCN (25 ml). The mixture was kept for 10 min at 0 °C and MeI (2.48 g, 0.017 mol) in anhydrous MeCN (2.5 ml) was added. After 30 min at 25 °C an inorganic precipitate was filtered off, and solvent and MeI were removed at 20 mmHg. Water (15 ml) was added and the mixture was extracted with  $\text{Et}_2\text{O}$  (3  $\times$  10 ml). Saturated aqueous sodium perchlorate (10 ml) was added to the aqueous layer. The precipitated perchlorate was washed with EtOH (2  $\times$  5 ml); it crystallised from  $\text{Me}_2\text{CO}$ -light petroleum as prisms (0.09 g, 3.5%), m.p. 90 °C (Found: C, 47.3; H, 5.9; N, 4.5.  $\text{C}_{12}\text{H}_{18}\text{ClNO}_8$  requires C, 46.8; H, 5.9; N, 4.5%).  $\nu_{\text{max}}$  (Nujol) 1 740 (C=O), 1 640 (C=N), and 1 070  $\text{cm}^{-1}$  (Cl-O);  $\delta$  ( $\text{CDCl}_3$ ; 100 MHz) 1.21 (9 H, s), 1.73 (3 H, d, *J* 6 Hz), 5.3 (1 H, q, *J* 6 Hz), and 8.7 (5 H, m).

1-[Dibenzyl-(*t*-butoxycarbonyl)methyl]pyridinium Bromide (22).—NaH (0.42 g, 0.017 mol) and benzyl bromide (2 g, 0.012 mol) in MeCN (5 ml) were added at 0 °C to the salt (3a) (2 g, 0.0087 mol) dissolved in MeCN (25 ml). The mixture was kept for 2 h at 0 °C. An inorganic precipitate was filtered off and the filtrate evaporated at 20 mmHg. The residue was triturated with  $\text{Et}_2\text{O}$  (4  $\times$  25 ml). The remaining solid was dissolved in  $\text{CHCl}_3$  and the solution filtered. Solvent was removed under reduced pressure, to give the bromide (22) as prisms ( $\text{Me}_2\text{CO}$ ) (2.84 g, 36%), m.p. 85–87 °C (Found: C, 65.9; H, 6.5; N, 3.0.  $\text{C}_{28}\text{H}_{28}\text{BrNO}_2$  requires C, 66.1; H, 6.2; N, 3.1%).  $\nu_{\text{max}}$  ( $\text{CHBr}_3$  film) 1 730 (C=O) and 1 630  $\text{cm}^{-1}$  (C=N);  $\delta$  ( $\text{CDCl}_3$ ; 100 MHz) 1.4 (9 H, s), 4.0 (2 H, d, *J* 14 Hz), 4.28 (2 H, d, *J* 14 Hz), 7.18 (10 H, m), 8.0 (2 H, t), 8.5 (1 H, t), and 9.1 (2 H, d).

Pyridinium  $\alpha$ -(*t*-Butoxycarbonyl)phenacylide (23).—NaH (0.21 g, 0.0087 mol) was added at 0 °C to the salt (3a) (1 g, 0.0044 mol) in MeCN (25 ml). The mixture was kept for 5 min at 0 °C. Benzoyl chloride (1.22 g, 0.0087 mol) in MeCN (25 ml) was added, and the mixture was stirred at 0 °C for 1 h. An inorganic precipitate was filtered off, and the filtrate was evaporated at 20 mmHg. The residue was

triturated with  $\text{Et}_2\text{O}$  (50 ml) and then recrystallised from EtOAc to yield the *ylide* (23) as yellow prisms (0.63 g, 50%), m.p. 185 °C (decomp.) (Found: C, 72.2; H, 6.2; N, 5.1.  $\text{C}_{18}\text{H}_{19}\text{NO}_3$  requires C, 72.7; H, 6.4; N, 4.7%).  $\nu_{\text{max}}$  ( $\text{HCBBr}_3$  film) 1 640–1 620 (C=O) and 1 570  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ; 100 MHz) 1.1 (9 H, s), 7.4 (5 H, m), 7.6–8.3 (3 H, m), and 8.75 (2 H, d);  $\lambda_{\text{max}}$  ( $\text{H}_2\text{O}$ ) 208 (log  $\epsilon$  4.23), 263 (4.18), and 350 nm (3.15); *m/e* 297 (50%) (base peak *m/e* 196).

1-(2-Benzoyloxy-2-phenyl-1-*t*-butoxycarbonylvinyl)pyridinium Perchlorate (24b).—NaH (0.21 g, 0.0088 mol) was added at 0 °C to the salt (3a) (1 g, 0.0044 mol) in MeCN (25 ml). After 10 min benzoyl chloride (1.22 g, 0.0087 mol) in anhydrous MeCN (5 ml) was added and the mixture kept at 20 °C for 1 h. The filtered solution was evaporated at 20 mmHg. Water (15 ml) was added and the mixture was extracted with  $\text{Et}_2\text{O}$  (3  $\times$  10 ml). The aqueous layer was evaporated at 20 mmHg (to 8 ml) and sodium perchlorate (1 g) was added. The precipitated perchlorate crystallised from  $\text{Me}_2\text{CO}$ -light petroleum as prisms (0.82 g, 37%), m.p. 142–143 °C (decomp.) (Found: C, 59.5; H, 5.0; N, 2.9.  $\text{C}_{25}\text{H}_{24}\text{ClNO}_8$  requires C, 59.8; H, 4.8; N, 2.8%).  $\nu_{\text{max}}$  (Nujol) 1 750 (ester C=O), 1 730 (unsat. ester C=O), 1 640 (C=N), and 1 100  $\text{cm}^{-1}$  (Cl-O);  $\delta$  [ $(\text{CD}_3)_2\text{CO}$ ; 60 MHz] 1.3 (9 H, s) and 7.5–9.5 (15 H, m); *m/e* 122 (100%) [ $\text{PhC}(\text{O})\text{O}^+ + \text{H}$ ].

1-Phenacylpyridinium Perchlorate (18b).—The perchlorate (24b) was heated at 160 °C under dry nitrogen for 1 h until gas evolution had ceased. The pyrolysate was dissolved in  $\text{Me}_2\text{CO}$ , reprecipitated with  $\text{Et}_2\text{O}$ , and recrystallised from EtOH to give the phenacyl perchlorate (0.09 g, 50%), m.p. 184–185 °C, identical with the specimen described above.

1-(1-*t*-Butoxycarbonyl-2-*p*-toluoyloxy-2-*p*-tolylvinyl)pyridinium Perchlorate (25b).—This was prepared similarly to (24b); after two crystallisations from EtOH it formed needles (25%), m.p. 164 °C (decomp.) (Found: C, 60.9; H, 5.2; N, 2.6.  $\text{C}_{27}\text{H}_{28}\text{ClNO}_8$  requires C, 61.2; H, 5.3; N, 2.6%).  $\nu_{\text{max}}$  ( $\text{HCBBr}_3$ ) 1 740 (C=O), 1 640 (C=N), and 1 080  $\text{cm}^{-1}$  (Cl-O);  $\delta$  ( $\text{CDCl}_3$ ; 100 MHz) 1.23 (9 H, s), 2.31 (3 H, s), 2.38 (3 H, s), 7.24 (4 H, m), 7.60 (2 H, d, *J* 8 Hz), 7.80 (2 H, d, *J* 8 Hz), 8.2 (2 H, d, *J* 6 Hz), 8.4 (1 H, t), and 9.0 (2 H, d, *J* 6 Hz); *m/e* 136 (57%) [*p*- $\text{MeC}_6\text{H}_4\text{C}(\text{O})\text{O}^+ + \text{H}$ ] and 119 (100%) [*p*- $\text{MeC}_6\text{H}_4\text{C}(\text{O})\text{O}^+$ ].

Pyridinium Dichloroacetyl-*t*-butoxycarbonylmethylide (26).—NaH (0.22 g) and dichloroacetyl chloride (0.6 g) were added to the salt (3a) (1 g) in MeCN (20 ml). After 0.5 h, the inorganic precipitate was filtered off. The filtrate was evaporated at 20 mmHg and the residue was triturated with  $\text{Et}_2\text{O}$  and then with water (30 ml). The *ylide* (26) (0.25 g) crystallised from EtOH as yellow prisms (0.19 g, 7.5%), m.p. 184 °C (decomp.) (Found: C, 50.9; H, 4.9; Cl, 23.2; N, 4.7.  $\text{C}_{13}\text{H}_{15}\text{Cl}_2\text{NO}_3$  requires C, 51.3; H, 5.0; Cl, 23.3; N, 4.6%).  $\nu_{\text{max}}$  ( $\text{HCBBr}_3$  film) 1 660–1 640 (C=O, C=N) and 1 570  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ; 100 MHz) 1.45 (9 H, s), 7.40–8.20 (4 H, m), and 8.42 (2 H, d, *J* 6 Hz);  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 275 (log  $\epsilon$  4.53) and 400 nm (3.68);  $\lambda_{\text{max}}$  (EtOH) 272 (log  $\epsilon$  4.49) and 368 nm (2.95).

We thank the Caulfield Institute of Technology, Caulfield East, Victoria, Australia, and the Department of Organic Chemistry, Institute of Chemistry, University, 90136 Łódź, Poland for leave of absence to J. B. and J. E., respectively. We are grateful to the Centre National de la Recherche Scientifique for a Scholarship (to B. P.).