2-(2-Nitrophenyl)oxaheterocycloniums: Potential Reagents for Oxidative Deamination of Primary Amines

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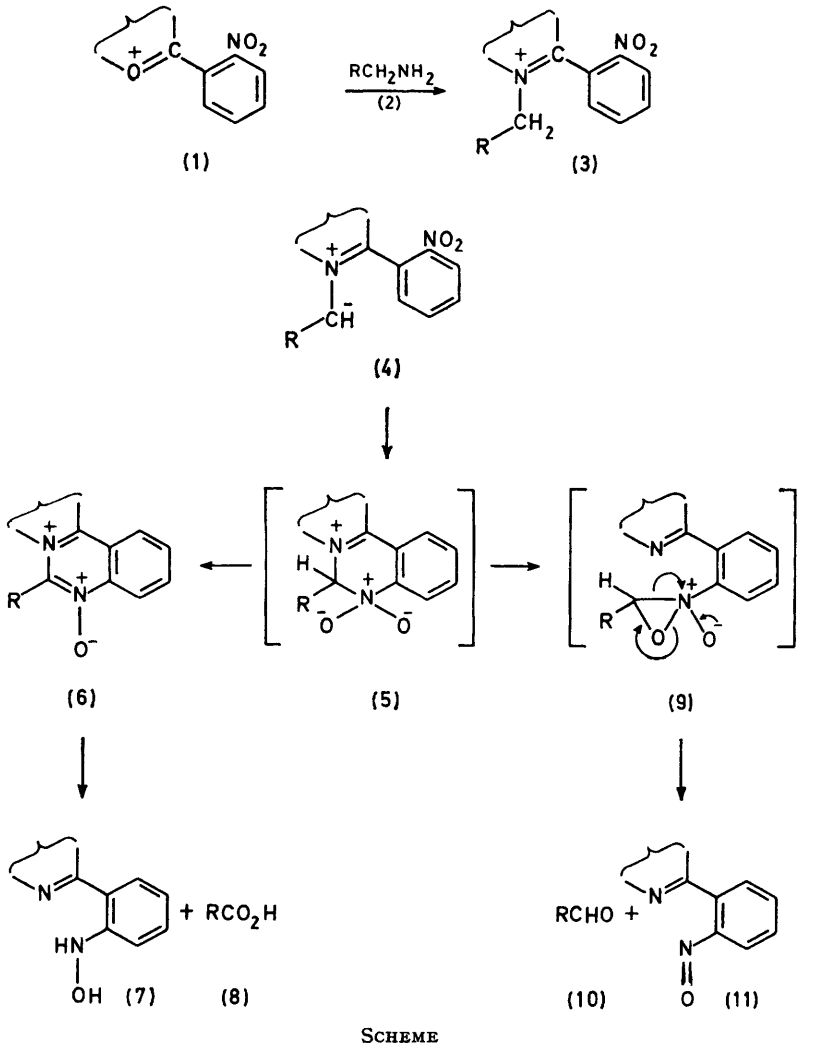
Pyridiniums from 2-(2-nitrophenyl)-4,6-diphenylpyrylium and benzylamines upon internal oxidation–reduction yield mixtures of benzaldehydes and benzoic acids.

PREVIOUS oxidative deaminations have relied on intermolecular reactions. Dehydrogenation to imines followed by hydrolysis gives carbonyl derivatives,[1] and of benzylamines to the nitrile followed by hydrolysis yields the acid.[2] Further, alkyl primary amines can be oxidised to nitriles by bromine,[3] iodine pentafluoride,[4] lead tetra-acetate,[5] and other reagents.[6]

N-Substituted 2,4,6-triphenylpyridiniums yield aldehydes on pyrolysis with sodium 1-oxido-4,6-diphenyl-2-pyridone[7] or by potassium dichromate under phase transfer conditions.[8] The first method avoids strong oxidising conditions, but requires fairly high temperatures and gives good yields only in the aromatic series. The second method is also restricted to the aromatic series: using more reactive 5,6-dihydro-2,4-diphenylbenzo[*h*]quinoliniums it gives good yields in refluxing dichloroethane.

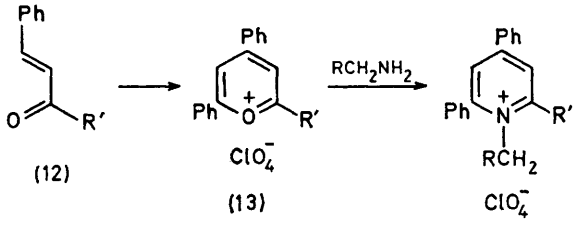
The concept behind the present work is outlined in Scheme 1: the oxaheterocyclonium (1) reacts with primary amine (2) to give azaheterocyclonium (3), the ylide (4) from which should cyclise into (5). This could either form the *N*-oxide (6) leading to hydroxylamine (7)



SCHEME

and acid (8) after base hydrolysis, or be converted into aldehyde (10) and nitroso-compound (11), *via* the rearranged product (9).

2-(2-*Nitrophenyl*)-4,6-*diphenylheterocycloniums*.—Attempted preparation [9] of 2-(2-nitrophenyl)-4,6-diphenylpyrylium (13) from chalcone and 2-nitroacetophenone gave only 2,4,6-triphenylpyrylium (by retro-aldolization [10]). However, 2′-nitrochalcone (12) and acetophenone in perchloric acid gave the desired pyrylium (13). Primary alkyl and aralkyl primary amines with pyrylium (13) in dichloromethane at 20 °C gave 1-substituted-2-(2-nitrophenyl)-4,6-diphenylpyridiniums (14a—j) (Table 1). Table 2 reports their i.r. and n.m.r. data.

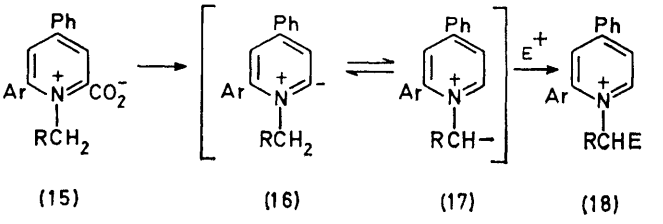


R′= *o*-$O_2NC_6H_4$

Cyclisation of the *N*-benzyl derivative (14a) into the *N*-oxide [*cf.* (6)] was unsuccessfully attempted as follows: (i) refluxing in piperidine (starting material recovered after 6 h), (ii) heating with triethyl phosphite at 100 °C (no change), (iii) photolysis (72 h) with or without oxygen in ethanol. However, methoxide in methanol at 40 °C gave an immediate precipitate of 2-(2-nitrosophenyl)-4,6-diphenylpyridine [*cf.* (11)]: benzaldehyde (44%) and benzoic acid (20%) were also isolated. The C, H, N analysis supported the identity of the nitrosopyridine which was distinct from 2-(2-nitrophenyl)-4,6-diphenylpyridine prepared from compound (13) with NH_3. The ^1H n.m.r. spectrum of 2-(2-nitrosophenyl)-4,6-diphenylpyridine showed only aromatic protons, including the characteristic 3,5-doublets for an unsymmetrically 2,4,6-trisubstituted pyridine. The i.r. spectrum showed no ν(NH), ν(6H), or ν(C=O).

The other expected pyridine derivative from Scheme 1 is 2-(2-hydroxylaminophenyl)-4,6-diphenylpyridine and a compound tentatively assigned this structure was also isolated.

The other benzyl derivatives (14b—f) reacted similarly to afford mixtures of the corresponding aldehydes and carboxylic acids (Table 3), indicating that both pathways



A; R = Ph

B; R = *o*-$O_2NC_6H_4$

of the Scheme were operative. Attempts to find conditions that led exclusively to aldehyde or exclusively to acid failed, as did attempts to recover either acid or aldehyde from the *N*-alkyl derivatives (14g—j).

6-*Ethoxycarbonyl*-2-(2-*nitrophenyl*)-4-*phenylheterocycloniums*.—1-Benzyl-4,6-diphenylpyridinium-2-carboxylates (15A) react with certain electrophiles at the α-carbon of the *N*-substituent with decarboxylation: [11] the zwitterions (16A) and (17A) are in equilibrium the latter giving products of the type (18).[12] Hence, 2-(2-nitrophenyl)-4-phenylpyridinium-6-carboxylate (15B) should form equilibrating zwitterions (16B) and (17B) to allow the subsequent cyclisation in (17B) (*cf.* enzyme reactions [13]).

Ethyl pyruvate with 2′-nitrochalcone (12) and BF_3·Et_2O at 50—60 °C (overheating leads to polymerisation) gave 2-(2-nitrophenyl)-4-phenyl-6-ethoxycarbonylpyrylium tetrafluoroborate, converted by benzylamine into the corresponding 1-benzylpyridinium. The betaine (15A; R = Ph) was obtained by basic hydrolysis. In THF under reflux this betaine decomposed into benzaldehyde (60%). Removal of one α-phenyl leads

TABLE 1

1-Substituted-2-(2-nitrophenyl)-4,6-diphenylpyridinium perchlorates (14a—j)

						Elemental analysis (%)					
						Required			Found		
R	No.	*t*/h	Yield (%)	M.p.[a] (°C)	Mol. formula	C	H	N	C	H	N
Benzyl	(a)	12	70	178—179	$C_{30}H_{23}ClN_2O_6$	66.3	4.2	5.1	66.1	4.1	5.0
2-Chlorobenzyl	(b)	12	88	186—187	$C_{30}H_{22}Cl_2N_2O_6$	62.4	3.8	4.8	62.3	3.7	4.8
3-Chlorobenzyl	(c)	12	80	151—152	$C_{30}H_{22}Cl_2N_2O_6$	62.4	3.8	4.8	62.1	3.7	4.7
4-Chlorobenzyl	(d)	12	70	166—168	$C_{30}H_{22}Cl_2N_2O_6$	62.4	3.8	4.8	62.4	4.2	4.6
4-Methylbenzyl	(e)	12	73	158—159	$C_{31}H_{25}ClN_2O_6$	66.8	4.5	5.0	66.5	4.8	4.8
3-Picolyl	(f)	12	85	183	$C_{29}H_{22}ClN_3O_6$	64.0	4.0	7.7	63.9	3.9	7.6
Me	(g)	3	70	227—230	$C_{24}H_{19}ClN_2O_6$	61.7	4.0	6.0	61.7	4.0	5.9
Et	(h)	6	70	245—247	$C_{25}H_{21}ClN_2O_6$	62.4	4.4	5.8	62.5	4.3	5.6
Bu^n	(i)	12	54	226—230	$C_{27}H_{25}ClN_2O_6$	63.7	4.9	5.5	63.8	4.9	5.3
$n\text{-}C_8H_{17}$	(j)	3	12	122—123	$C_{31}H_{33}ClN_2O_6$	65.9	5.8	4.9	65.8	5.8	4.9

[a] Plates, from EtOH.

TABLE 2

I.r.[a] and n.m.r.[b] spectra of 1-substituted-2-(2-nitrophenyl)-4,6-diphenylpyridinium perchlorates (14)

N-Substituent	$\nu_{max.}$ Py$^+$	$\nu_{max.}$ $-NO_2$	$\nu_{max.}$ Others	Chemical shift (δ) Aliphatic protons N-CH_2[c]	Aliphatic protons Others	Aromatic protons 3,5-H[d]	Aromatic protons Others
Benzyl	1 623s	1 525s, 1 350s	1 566s, 1 155s, 888s, 788s, 771s, 760s	5.35—5.85		8.19 (1 H) 8.32 (1 H)	6.65 (2 H, m) 7.28 (2 H, m) 7.7—8.0 (14 H m,) 8.5 (1 H, m)
2-Chlorobenzyl	1 625s	1 530s, 1 350s	1 570m, 790w, 754s	5.5—6.0		8.2 (1 H) 8.3 (1 H)	6.8 (1 H, m) 7.2 (2 H, d, *J* 4 Hz) 7.7—8.0 (14 H, m) 8.5 (1 H, m)
3-Chlorobenzyl	1 624s	1 530s, 1 350s	1 565m, 893m, 792m, 778s, 762s	5.3—5.7		8.1—8.3 (2 H, m)	6.5 (2 H, m) 7.2 (2 H, m) 7.7—7.9 (13 H, m) 8.5 (1 H, m)
4-Chlorobenzyl	1 622s,	1 528s, 1 342s	1 608m, 1 575m, 1 492s, 1 012m, 897m, 795s, 769s	5.4—5.9		8.3 (1 H) 8.4 (1 H)	6.7 (2 H, d, *J* 8 Hz) 7.2 (2 H, d, H 8 Hz) 7.7—8.0 (13 H, m) 8.6 (1 H, m)
4-Methylbenzyl	1 623s	1 530s 1 348s	1 610s, 1 575m, 795m, 762m, 745m	5.3—5.75	2.3 (3 H, s)	8.1 (1 H) 8.2 (1 H)	6.5 (2 H, d, *J* 8 Hz) 7.0 (2 H, d, *J* 8 Hz) 7.6—7.9 (13 H, m) 8.4—8.5 (1 H, m)
3-Picolyl	1 619s	1 527s, 1 343s	1 580m, 1 555m, 1 427m, 792s, 767s, 755m	5.8—6.4 (2 Hm,m)		*e*	7.7 (9 H, m) 8.1 (7 H, m) 8.4 (3 H, m) 8.8 (1 H, m)
Me	1 630s	1 530s, 1 350s	1 575s, 1 450m, 890s, 760s	3.9 (3 H, s)		8.1 (1 H) 8.2 (1 H)	7.6—7.9 (13 H, m) 8.5 (1 H, m)
Et	1 630s	1 530s, 1 350s	1 570m, 1 418m, 798m, 770s, 753s	4.1—4.7 (2 H, m)	0.95—1.6 (3 H, m)	8.1 (1 H) 8.2 (1 H)	7.6—7.9 (13 H, m) 8.6 (1 H, m)
Bu^n	1 630s,	1 530s, 1 350s	1 600m, 1 575m, 1 470m, 892s, 795s, 713s	4.0—4.5 (2 H, m)	1.6—1.75 (2 H, m) 0.5—1.05 (5 H, m)	8.1 (2 H, m)	7.6—7.8 (13 H, m) 8.6—8.8 (1 H, m)
n-C_8H_{17}	1 625s	1 530s, 1 350s	1 575m, 767m	4.1—4.6 (2 H, m)	1.0—1.7 (15 H, m)	8.1 (2 H, m)	7.6—7.8 (13 H, m) 8.6 (1 H, m)

[a] Recorded in $CHBr_3$ mull: s = strong, m = medium, w = weak. [b] Solvent: CF_3CO_2H: 60 MHz. [c] 2 H, q, *J* 15 Hz unless otherwise indicated. [d] d *J* 2 Hz unless otherwise indicated. [e] Overlapped by other signals in region δ 8.1—8.8.

apparently to the oxaziridine mode of reaction rather than to the *N*-oxide and hence benzoic acids.

2-(2-*Nitrophenyl*)-3,4,5-*triphenylimidazoliums*.—Failure to isolate the cyclic *N*-oxide (6) derived from 1-substituted 2-(2-nitrophenyl)-4,6-diphenylpyridiniums may be due to their instability (ease of hydrolysis) caused by steric crowding. Hence, the less reactive [14] imidazolium derivative (23) was prepared.

N-(α-Benzoylbenzyl)aniline (19) [15] and 2-nitrobenzoyl chloride gave the corresponding *N*-(2-nitrobenzoyl)-aniline (20) which was cyclised by H_2SO_4–$NaClO_4$ into 2-(2-nitrophenyl)-3,4,5-triphenyloxazolium (21). Benzylamine with the oxazolium (21) gave 1-benzyl-4,5-dihydro-5-hydroxy-2-(2-nitrophenyl)-3,4,5-triphenylimidazolium (22), which was dehydrated by sulphuric acid into *N*-benzylimidazolium (23).

In NaOMe–MeOH under reflux the imidazolium (23) cyclised into the *N*-oxide (24). I.r. showed the loss of the NO_2 bands at 1 530 and 1 350 cm^{-1} of (23) and appearance of the *N*-oxide band at 1 250 cm^{-1} in (24). The ^1H n.m.r. spectrum showed a multiplet in the region δ 6.8—7.6. In the u.v. region a bathochromic shift from

TABLE 3

Reaction of 1-substituted 2-(2-nitrophenyl)-4,6-diphenylpyridinium perchlorates (14) with sodium methoxide

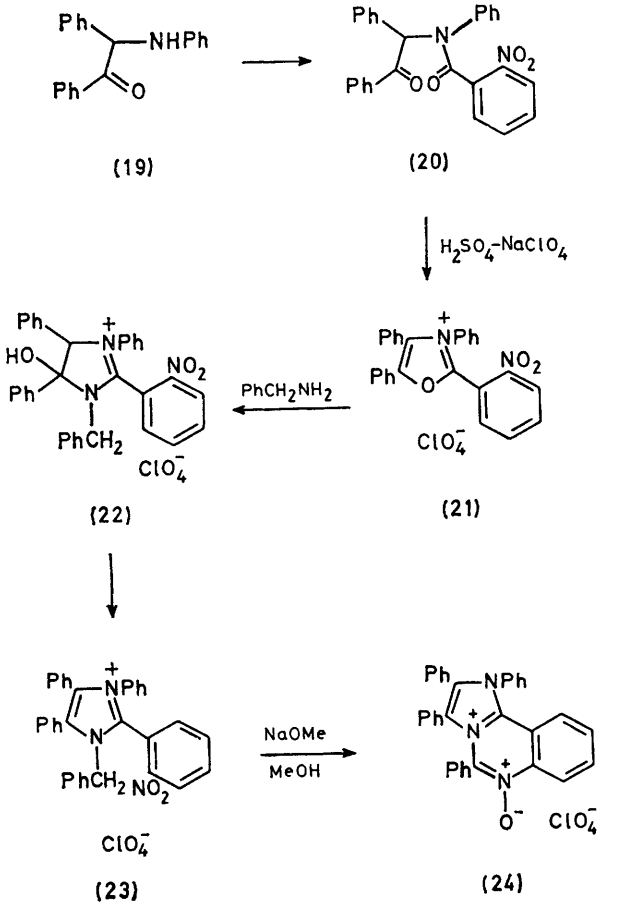
	Aldehyde (RCHO)			Carboxylic acid (RCO_2H)		
		DNP derivative				
R	Yield (%)	M.p. (°C)	Lit. m.p. (°C)	Yield (%)	M.p. (°C)	Lit. m.p. (°C)
Phenyl	44	235	235 [a]	20	122	122.4 [e]
2-Chlorophenyl	35	211	209 [b]	20	142	142 [f]
3-Chlorophenyl	35	252	256 [b]	20	156	158 [f]
4-Chlorophenyl	40	270	270 [b]	20	244	243 [f]
4-Methylphenyl	30	230	232.5—234.5 [c]	15	182	182 [g]
3-Pyridyl	15	258	259 [d]			

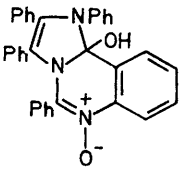
[a] Ref. 18. [b] J. J. Blanksma and M. L. Wackers, *Recl. Trav. Chim. Pays-Bas*, 1936, **55**, 655. [c] Harold H. Strain, *J. Am. Chem. Soc.*, 1935, **57**, 758. [d] S. J. Angyal, G. B. Barlin, and P. C. Wallis, *J. Chem. Soc.*, 1953, 1740. [e] 'Handbook of Chemistry and Physics,' 57th edn., ed. R. C. Weast, CRC Press, Cleveland, Ohio, U.S.A., 1976, p. C-180. [f] Footnote *e*, p. C-187. [g] Footnote *e*, p. C-196.

λ 250 nm in (23) to λ 375 nm as expected for (24) was observed.

Attempts to open the *N*-oxide (24) to give benzoic acid failed: reaction with NaOH–EtOH gave the hydroxy-adduct (25), usually mixed with unchanged compound (24).

Conclusions.—The feasibility of intramolecular reaction of 2-*o*-nitrobenzylpyridiniums has been demonstrated. However, the simultaneous formation of aldehydes and acids from benzylamines and the stability of the imidazole derivative (24) indicate that the development of a satisfactory general synthetic procedure awaits further experimentation.





(25)

EXPERIMENTAL

M.p.s. were determined with a Reichert apparatus and are uncorrected. ^1H N.m.r. spectra were recorded with a Perkin-Elmer R-12 spectrophotometer using internal $SiMe_4$ as a standard. I.r. spectra were obtained on a Perkin-Elmer 257 spectrophotometer.

The following compounds were prepared using literature data: 2′-nitroacetophenone (70%), b.p. 119—121 °C/0.5—1.0 mmHg (lit.,[15] b.p. 158.5—159 °C/16 mmHg), 2′-nitrochalcone (90%), m.p. 124 °C (lit.,[16] m.p. 128—129 °C), *N*-(α-benzoylbenzyl)aniline (19) (65%), m.p. 97—98 °C (lit.,[17] m.p. 97.5—99 °C).

2-(2-*Nitrophenyl*)-4,6-*diphenylpyrylium Perchlorate* (13).—$HClO_4$ (70%) (10.00 ml) was added dropwise to a stirred suspension of 2′-nitrochalcone (5.0 g, 20 mmol) and acetophenone (2.5 g, 20 mmol). The mixture was heated on a steam-bath for 2 h, cooled, and added to Me_2CO (15 ml). The resulting solid was filtered off and washed with Et_2O. The filtrate was diluted with Et_2O (1 l) to give further crops of product. The combined crude product was crystallised from HOAc to give 2-(2-*nitrophenyl*)-4,6-*diphenylpyrylium perchlorate* (13) (4.5 g, 50%) as greenish-yellow needles, m.p. 227—230 °C (Found: C, 61.0; H, 3.5; N, 3.0. $C_{23}H_{16}ClNO_7$ requires C, 60.8; H, 3.5; N, 3.0%); $\nu_{max.}$ (Nujol) 1 629s, 1 603m, 1 591s, 1 579m, 1 520s, broad, 1 418m, 1 400w, 1 350m, 1 322m, 1 193m, 1 080s, broad, 994m, 768s, and 665s; δ(CF_3CO_2H) 7.82 (5 H, m), 8.12—8.31 (9 H, m), 8.47 (1 H, d, *J* 3 Hz), and 8.82 (1 H, d, *J* 3 Hz).

2-(2-*Nitrophenyl*)-4,6-*diphenylpyridine*.—Dry ammonia gas was passed for 0.5 h through a suspension of 2-(2-nitrophenyl)-4,6-diphenylpyrylium perchlorate (1.0 g, 2.2 mmol) in EtOH (20 ml). The solvent was then evaporated and the residue extracted with CH_2Cl_2. Evaporation and crystallisation from 95% EtOH gave the *pyridine* (0.54 g, 70%) as needles, m.p. 220 °C (Found: C, 78.3; H, 4.6; N, 7.8. $C_{23}H_{16}N_2O_2$ requires C, 78.4; H, 4.5; N, 7.9%); $\nu_{max.}$ ($CHBr_3$) 1 612m, 1 598s, 1 550s, 1 530s, 1 500m, 1 450m, 1 400m, 1 350s, 1 030w, 980m, 788m, and 760s; δ($CDCl_3$) 7.3—7.6 (12 H, m) and 7.9—8.1 (4 H, m).

General Procedure for the Preparation of 1-*Substituted* 2-(2-*Nitrophenyl*)-4,6-*diphenylpyridinium* (14) *Perchlorates*.—The appropriate amine (4.4 mmol) was added dropwise to a stirred suspension of 2-(2-nitrophenyl)-4,6-diphenylpyrylium perchlorate (2.00 g, 4.4 mmol) in CH_2Cl_2 (25 ml). The mixture was stirred overnight. Addition of an excess of Et_2O gave the title compound (see Table 1).

General Procedure for the Decomposition of 1-*Substituted* 2-(2-*Nitrophenyl*)-4,6-*diphenylpyridinium Perchlorates* (14).—The title compound was added in MeOH containing an equimolar amount of NaOMe. The solution was warmed up to 35 °C, stirred for 2 h at 20 °C, and then filtered to give 2-(2-*nitrosophenyl*)-4,6-*diphenylpyridine* which crystallised from EtOH as hexagonal crystals (*ca.* 60%), m.p. 173—175 °C (Found: C, 82.0; H, 4.7; N, 8.0. $C_{23}H_{16}N_2O$ requires C, 82.1; H, 4.7; N, 8.3%); $\nu_{max.}$ ($CHBr_3$) 1 610m, 1 595s, 1 548s, 1 403s, 1 276s, 885m, 760s, and 730m; δ(CF_3CO_2H) 6.7 (1 H, d, *J* 9 Hz), 7.7—8.3 (14 H, m), 8.5 (1 H, d, *J* 2 Hz), and 8.6 (1 H, d, *J* 2 Hz). The filtrate was evaporated and the residue washed with light petroleum (b.p. 60—80 °C). Evaporation of light petroleum gave the aldehyde which was isolated as a dinitrophenyl derivative. The residue was then washed with H_2O and the washings acidified with 4N-HCl to give the carboxylic acid. Finally the residue was dissolved in CH_2Cl_2 and dried over $MgSO_4$. Evaporation of the solvent gave 2-(2-*hydroxyaminophenyl*)-4,6-*diphenyl-pyridine* which crystallised from EtOH as plates (*ca.* 40%), m.p. 270—272 °C (Found: N, 8.2. $C_{23}H_{18}N_2O$ requires N, 8.3%); $\nu_{max.}$ ($CHBr_3$) 1 611m, 1 595s, 1 548s, 1 469m, 1 402m, 876m, 760s, and 745 cm^{-1}; δ(CF_3CO_2H) 7.1 (13 H, m) and 7.7—8.2 (3 H, m).

2-*Ethoxycarbonyl*-6-(2-*nitrophenyl*)-4-*phenylpyrylium Tetrafluoroborate*.—2′-Nitrochalcone (0.5 g, 2 mmol), ethyl pyruvate (0.5 g, 4 mmol), and boron trifluoride–diethyl ether (2.0 ml) were warmed at 40—50 °C for 2 h. The mixture was then dropped into rapidly swirling Et_2O (250 ml) to give 2-*ethoxycarbonyl*-6-(2-*nitrophenyl*)-4-*phenylpyrylium tetrafluoroborate* (0.25 g, 30%) which crystallised from Me_2CO as yellow needles, m.p. 174—175 °C (Found: C, 55.0; H, 3.5; N, 3.0. $C_{20}H_{16}BF_4NO_5$ requires C, 54.9; H, 3.6; N, 3.2%); $\nu_{max.}$ ($CHBr_3$) 1 746s, 1 630s, 1 591s, 1 540s, 1 470m, 1 362m, 1 050s, 952s, 779s, and 720s; δ(CF_3CO_2H) 1.3—1.5 (3 H, t, *J* 6 Hz), 4.5—4.8 (2 H, q, *J* 8 Hz), 7.9—8.4 (9 H, m), 8.8 (1 H, s), and 9.1 (1 H, s).

1-*Benzyl*-2-*ethoxycarbonyl*-6-(2-*nitrophenyl*)-4-*phenylpyridinium Tetrafluoroborate*.—Benzylamine (0.16 g, 1.5 mmol) was added to a suspension of 2-ethoxycarbonyl-6-(2-nitrophenyl)-4-phenylpyrylium tetrafluoroborate (0.6 g, 1.3 mmol) in CH_2Cl_2 (20 ml). The red solution was stirred for 3 h. Addition of an excess of Et_2O gave a gum which crystallised from EtOAc to give the title *compound*; this recrystallised from EtOH (0.42 g, 70%) as plates, m.p. 188 °C (Found: C, 61.8; H, 4.4; N, 5.3. $C_{27}H_{23}BF_4N_2O_4$ requires C, 61.6; H, 4.4; N, 5.3%); $\nu_{max.}$ ($CHBr_3$) 1 735s, 1 618s, 1 592s, 1 530s, 1 050s, 796s, and 769s; δ(CF_3CO_2H) 1.3 (3 H, m), 4.4 (2 H, m), 5.9 (2 H, q, *J* 8 Hz), 7.0 (2 H, m), 7.4 (2 H, m), 7.7—8.0 (9 H, m), and 8.3—8.7 (3 H, m).

1-*Benzyl*-6-(2-*nitrophenyl*)-4-*phenylpyridinium*-2-*carboxylate* (15B; R = Ph).—1-Benzyl-2-ethoxycarbonyl-6-(2-nitrophenyl)-4-phenylpyridinium tetrafluoroborate (0.55 g, mmol) was suspended in H_2O and to it an equivalent amount of NaOH (0.05 g) in water (0.5 ml) was added. The solution was stirred for 24 h and then filtered to give the *title compound* (0.4 g, 93%) as plates, m.p. 120—121 °C (Found: N, 6.4. $C_{25}H_{18}N_2O_4$ requires N, 6.8%); $\nu_{max.}$ ($CHBr_3$) 1 655s, 1 620s, 1 608s, 1 592s, 1 530s, 1 500m, 1 475m, 1 345s, 1 270m, 1 240m, 1 039w, 1 028w, 1 000w, 902w, 836w, 815w, and 790w; δ($CDCl_3$) 5.8 (2 H, m), 6.8—7.0 (4 H, m), 7.5—7.7 (9 H, m), and 8.2—8.4 (3 H, m).

Decomposition of 1-*Benzyl*-6-(2-*nitrophenyl*)-4-*phenylpyridinium*-2-*carboxylate* (15B; R = Ph) *in THF*.—The betaine (1.0 g, 2.4 mmol) was refluxed in anhydrous THF (15 ml) for 3 h. THF was removed under reduced pressure (25 mmHg): the residue in MeOH (3 ml) was treated with 2,4-dinitrophenylhydrazine (0.50 g, 2.5 mmol) in MeOH (15 ml) and conc. H_2SO_4 (1 ml) to give benzaldehyde 2,4-dinitrophenyl hydrazone (0.46 g, 60%), m.p. 235 °C (lit.,[18] m.p. 235 °C).

N-(α-*Benzoylbenzyl*)-N-(2-*nitrobenzoyl*)*aniline* (20).—*N*-(α-Benzoylbenzyl)aniline (19) (2.0 g, 7 mmol) was suspended in 10% NaOH solution (100 ml) and *o*-nitrobenzoyl chloride (1.45 g, 8 mmol) was added dropwise with vigorous stirring. The crude product was filtered off and crystallised from EtOH to give N-(2-*nitrobenzoyl*)*aniline* (20) (2.1 g, 70%) as plates, m.p. 191—192 °C (Found: C, 74.0; H, 4.8; N, 6.4. $C_{27}H_{20}N_2O_4$ requires C, 74.3; H, 4.6; N, 6.4%); $\nu_{max.}$ ($CHBr_3$) 1 688m, 1 640s, 1 598m, 1 446m, 1 342m, 855s, 790s, and 742s; δ(CF_3CO_2H) 5.5 (1 H, s), 7.1—7.5 (17 H, m), and 8.05—8.15 (2 H, m).

2-(2-*Nitrophenyl*)-3,4,5-*triphenyloxazolium Perchlorate* (21).—*N*-(α-Benzoylbenzyl)-*N*-(2-nitrobenzoyl)aniline (20) (1.0 g, 2 mmol) was mixed with concentrated H_2SO_4. Addition of cold water (100 ml) gave 2-(2-*nitrophenyl*)-3,4,5-*triphenyloxazolium* which was isolated as the perchlorate (21); this crystallised from Pr^iOH–EtOH as hexagonal crystals (1.1 g, 90%), m.p. 204.5—205.5 °C (Found: C, 62.1; H, 3.6; N, 5.3. $C_{27}H_{19}ClN_2O_7$ requires C, 62.5; H, 3.6; N, 5.4%); $\nu_{max.}$ ($CHBr_3$) 1 650m, 1 535s, 1 489s, 1 445s, 1 350s, 1 080s, 957m, 770s, and 740s; δ(CF_3CO_2H) 7.42—7.52 (15 H, m) and 8.05—8.5 (4 H, m).

1-*Benzyl*-2-(2-*nitrophenyl*)-3,4,5-*triphenylimidazolium Perchlorate* (23).—Benzylamine (0.41 g, 3.8 mmol) was added to a suspension of 2-(2-nitrophenyl)-3,4,5-triphenyloxazolium perchlorate (1.0 g, 2 mmol) in EtOH (20 ml). The mixture was stirred for 12 h at 20 °C after which needles of the resulting intermediate, 1-*benzyl*-4,5-*dihydro*-5-*hydroxy*-2-(2-*nitrophenyl*)-3,4,5-*triphenylimidazolium perchlorate* (22) were filtered off (1.0 g, 83%); it had m.p. 209 °C (Found: C, 65.0; H, 4.4; N, 6.7. $C_{34}H_{28}ClN_3O_7$ requires C, 65.2; H, 4.4; N, 6.7%); $\nu_{max.}$ ($CHBr_3$) 3 410m (OH str), 1 622w, 1 568s, 1 533s, 1 450s, 1 350s, 1 110s, 1 080s, 1 045s, and 760s; δ(CF_3CO_2H) 4.6 (2 H, s), 6.4—6.7 (3 H, m), 7.1—7.35 (13 H, m) and 7.7—8.2 (9 H, m). Treatment of this intermediate with concentrated H_2SO_4 followed by cold water gave the *title compound* (0.92 g, 78%) which crystallised from isopropyl alcohol as hexagonal crystals, m.p. 185 °C (Found: C, 66.9; H, 4.3; N, 6.8. $C_{34}H_{26}ClN_3O_6$ requires C, 67.1; H, 4.3; N, 6.9%); $\nu_{max.}$ ($CHBr_3$) 1 618w, 1 530s, 1 480m, 1 350s, 1 080s, 925w, 790m, 768m, and 750s; δ($CDCl_3$) 5.08—5.41 (2 H, q, *J* 15 Hz), 6.9 (2 H, m), 7.3 (15 H, m), 7.8 (5 H, m), and 8.7 (1 H, d, *J* 8 Hz).

Reaction of 1-*Benzyl*-2-(2-*nitrophenyl*)-3,4,5-*triphenylimidazolium Perchlorate* (23) *with Sodium Methoxide*.—1-Benzyl-2-(2-nitrophenyl)-3,4,5-triphenylimidazolium perchlorate (0.9 g, 1.5 mmol) was dissolved in MeOH (25 ml) containing NaOMe (0.16 g, 3 mmol). The solution was refluxed for 12 h, cooled, and acidified to give 6-*oxido*-1,2,3,5-*tetraphenyl*-1H-*imidazo*[1,2-c]*quinazolin*-4-*ium perchlorate* (24) which crystallised from MeOH (0.6 g, 70%)

as plates, m.p. 175—180 °C (Found: C, 68.8; H, 4.6; N, 7.1. $C_{34}H_{29}ClN_3O_5$ requires C, 69.2; H, 4.9; N, 7.1%); $\nu_{max.}$ ($CHBr_3$) 1 592s, 1 577w, 1 495s, 1 450w, 1 245m, 1 080s, 997w, and 755m; δ($CDCl_3$) 6.8—7.6 (24 H, m); $\lambda_{max.}$ (EtOH) 375 (ε 6 063).

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