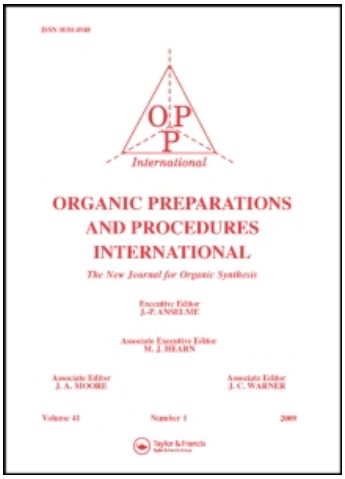

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AN IMPROVED METHOD FOR THE PREPARATION OF 4-ARYL-2,6-DIPHENYLPYRYLIUM PERCHLORATES AND THEIR REACTION WITH AMMONIA AND METHYLAMINE

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AN IMPROVED METHOD FOR THE PREPARATION OF 4-ARYL-2,6-DIPHENYLPYRYLIUM PERCHLORATES AND THEIR REACTION WITH AMMONIA AND METHYLAMINE

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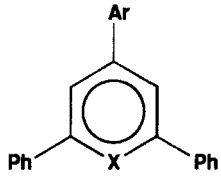
The extraordinary variety of the transformations of pyrylium salts makes them good and widely applicable synthons. Their major advantage is the very facile *oxygen* to *nitrogen* exchange to give pyridines and pyridinium salts. The present paper shows that 4-aryl-2,6-diphenylpyrylium



1 - 3

1 X = $\overset{+}{O}$ ClO_4^-

2 X = N

3 X = $\overset{+}{N}$Me ClO_4^-

a) R = C_6H_5 b) R = 4-MeC_6H_4

c) R = 4-$Me_2NC_6H_4$ d) R = 4-$MeOC_6H_4$

e) R = 4-$MeSC_6H_4$ f) R = 4-$F_3CC_6H_4$

g) R = $4FC_6H_4$ h) R = 4-ClC_6H_4

i) R = 4-BrC_6H_4 j) R = 4-$O_2NC_6H_4$

k) R = 4-$MeOCOC_6H_4$ l) R = 3-ClC_6H_4

m) R = 3-$O_2NC_6H_4$ n) R = 2-ClC_6H_4

perchlorates (**1**) are highly efficient precursors for a wide series of 4-aryl-2,6-diphenylpyridines (**2**) and of the corresponding 1-methylpyridinium perchlorates (**3**).

The reported methods[2-18] for the preparation of **1** are not quite satisfactory because of long synthetic sequences[2-8] or of low yields[9-18] in the case of one-step process. Thus, pyrylium salts **1a**,[2-5] **1d**,[4-6] **1j**[5] and **1m**[7] have been obtained in the two-step synthesis from the corresponding substituted benzylideneacetophenones. On the other hand, **1a**, **1d** and **1j** were prepared in a multi-step process from the corresponding aldehyde diacetates with trityl perchlorate and acetophenone.[8] Although **1a**,[12-15] **1b**,[15-16] **1c**,[14,15] **1d**,[12,13,15,16] **1g-1i**,[17] **1j**,[14,16] **1m**[14] and **1n**[18] derivatives are formed directly from substituted benzaldehydes and acetophenone, the reaction conditions and the yields reported are not

uniform. Thus, various condensing agents such as H_2SO_4 ($HClO_4$) or $POCl_3$ ($HClO_4$),[12] $FeCl_3$ ($HClO_4$)[13], $HClO_4$,[14,16] BF_3[15,18] as well as Ac_2O/AcOH ($HClO_4$)[17] were used. The yields are as follows: **1a** (49%, 40%),[14,15] **1b** (27% and 41%),[15,16] **1c** (33%),[14] **1d** (44%),[15,16] **1g** (28%),[17] **1h,i** (31%),[17] **1j** (27%),[14] **1m** (31%)[14] and **1n** (26%);[18] for compounds **1a,d**[12,13] and **1c**[15] the yield was not specified and the isolation of **1j** involves a tedious work-up. The preparation of **1a** and **1c** involves different reactions. Thus, **1a** was obtained from α-methylstyrene and benzoyl chloride in the presence of $AlCl_3$ in 9% yield,[9] while **1c** was formed from 2,6-diphenylpyran-4-one or 2,6-diphenylpyrylium perchlorate with N,N-dimethylaniline in the presence of $POCl_3$ (no yield given)[10] and Ac_2O in 36% yield,[11] respectively. Moreover, it should be mentioned that melting points of the compounds obtained by various authors differ substantially (see Table 1). This indicates that a general procedure affording a comprehensive range of derivatives of 1 of high quality and in reasonably good yields would be desirable.

TABLE 1. Preparation of 4-Aryl-2,6-Diphenylpyrylium Perchlorates (1)[a]

Cmpd No.	Yield (%)	mp (°C)	lit. mp (°C)	Solvent for cryst.	Time (hrs)
1a[b]	53	270-273	290,[3] 293-295,[4] not given,[5] 265,[8] 271,[12] 214-215,[13] 273,[14] 253-255[15]	EtOH	2
1b	46	295-296	283-284,[15] 288[16]	$CHCl_3$-MeOH (1:5)	1.5
1c	51	>330	>300,[10,11] 360[14]	$MeNO_2$	3
1d	54	269-270	256,[8,16] 235-236[13] 252-253,[15] 257-258[12]	$CHCl_3$-MeOH (1:4)	1.5
1e[b]	51	267-269	–	$CHCl_3$-MeOH (1:4)	1
1f	45	282-284	–	$MeNO_2$	1.5
1g	47	246-248	283[17]	$MeNO_2$	1.5
1h	46	313-314	296[17]	$MeNO_2$	1.5
1i	42	274-275	319[17]	$MeNO_2$	1.5
1j	42	300-301	>300,[5] 299,[8] 302,[14] 296[16]	$MeNO_2$	2
1k	33[c]	335-337	–	$MeNO_2$	2.5
1l	58	295-297	–	MeOH	3
1m	38	285-287	241-242,[5] 268,[7] 224.5-225[14]	$MeNO_2$	3
1n	37	114-115	114-116[18]	MeOH	2.5

a) Method B except for **1a** and **1c**. b) Method A. c) Partial hydrolysis of CO_2Me group was observed.

We now report that compounds **1c-1n** are best prepared, in a one-step process starting from the corresponding benzaldehydes (1 equiv) and acetophenone (2 equiv) in the presence of perchloric acid (2 equiv) as the cyclizing reagent, alhough for **1a** and for **1c**, the yield is much higher when sulfuric acid is used. A simple increase in the quantity of both solvent and condensing agent allows the final product to be obtained in high quality. Although the reactions do not proceed quantitatively (see Table 1), their yields usually exceed those reported for other one-step syntheses.[9,12-17]

Recently, we needed 4-aryl-2,6-diphenylpyridines (**2**) and the respective 1-methylpyrydinium perchlorates (**3**), bearing a wide variety of functional groups as precursors of supramolecular compounds and dyes. Derivatives **2a**,[14,15,19] **2b,d**,[15] **2c**,[14] **2g-2i**,[17] **2j**,[14] **2m**[7,14] and **2n**[18] were obtained earlier from the reaction of **1** with ammonia. The reaction conditions[7,17,18] were not described except for **2a-2d** (room temperature, 6 hrs). The yields were given only for **2a** (89%)[14] and **2n** (67%).[18] Moreover, **2a**, **2d** and **2h** were obtained from acetophenone, benzaldehyde and ammonia or hydroxylamine hydrochloride under high pressure in a 36%, 11% and 18-32% yield,[20] respectively. Derivatives **2a-2d**, **2h** and **2j** may be synthesized in a multi-step synthesis starting from N-(diphenylphosphinyl)-1-azaallyl anions and α,β-unsaturated carbonyl compounds.[18,21] It should be mentioned that **2a**, **2c** and **2d** can also be prepared in a one-step reaction from the substituted benzaldehyde, acetophenone and ammonium acetate in acetic acid in satisfactory yields (64-68%).[22] We have found, however, that this procedure fails when *m*- and *p*-nitro-, *o*- and *m*-chloro- and *p*-methoxycarbonylbenzaldehydes are used. Moreover, tarry products, not suited for easy purification, were formed in the synthesis of **2e** and **2f**. Therefore, the method described in Experimental Section (50 equiv of ammonia, 50°, 0.5-2 hrs) is useful for the preparation of the wide range of **2**, except for **2n** whose synthesis requires a longer reaction time. As expected, 4-carbamoyl-2,6-diphenylpyridine is formed from **1k** and ammonia (see Table 2).

Although procedures to convert 2,4,6-triphenylpyrylium into corresponding 1-substituted pyrydinium salts (**3**) have been described,[3,23,24] the compounds studied here are for the most part unknown. As reported, only two such salts, *i.e.* **3a**[3,24-26] and **3c**,[12,27] were obtained earlier under different reaction conditions. Thus, gaseous methylamine was used in some cases[25] and a two-step process involving the formation of thiopyrylium salts was proposed.[27] Although the ring nitrogen atom of **2** cannot be easily quaternized due to the steric hindrance by two neighboring phenyl rings,[26] compound **3a** was found to be a product of methylation of the respective pyridine;[26] these procedures do not report yields.[12,26,27] The study of numerous literature synthetic approaches and testing the procedures optimized by ^{13}C NMR method[23] for 1-substituted 2,4,6-triphenylpyridininium salts allowed us to extend the reported methodology[3,23] for a wide series of **3** (see Experimental Section). Thus, since the yields and type of the products obtained in the reaction of pyrylium salts with amines depend on the ratio of substrates, temperature, reaction time and counter anion, the application of the mentioned procedure[3,23] (1 equiv of pyrylium salt and 2 equiv of primary amine, 0.3-70 hrs, room temperature) requires some precautions. The formation of demethylation products, *i.e.*, the

TABLE 2. Preparation of 4-Aryl-2,6-Diphenylpyridines (2)

Cmpd No.	Yield (%)	mp. (°C)	lit. mp. (°C)	Solvent for cryst.	Time (hrs)
2a	90	135-136	138,[14,19] 136-137,[15] 134-135,[18] 137-138,[20] 141-142,[21] 139[22]	EtOH	0.5
2b	58	121-123	118-118.5,[15] 119-122.5[21]	EtOH	1.5
2c	64	126-127	138,[14,22] 142-143[18]	EtOH-$CHCl_3$(1:1)	2
2d	70	101.5-102	99-100,[15,18,21] 99.5-100,[20] 102[22]	MeOH	1
2e	63	99.5-100.5	–	MeOH	1
2f	51	144-145	–	EtOH	1.5
2g	81	141-142	137-138[17]	EtOH	1.5
2h	66	129-130.5	129-130,[17,18] 128.5-130,[20] 127-131.5[21]	EtOH	1
2i	72	132.5-134	131-132[17]	EtOH	1.5
2j	57	202-203	187.5,[14] 202-203[18]	MeOH-$CHCl_3$(1:1)	2
2k	5[a]	159-161	–	EtOH	1
2l	54	122-123	–	MeOH	1
2m	52	153.5-155	150-151,[7] 152.5-153[14]	EtOH	1
2n	65	113-114	114-115[18]	MeOH	24

a) The primary product, *i.e.* the ester, was transformed mostly into the corresponding amide [mp. 230-232° (EtOH)]. ^{1}H NMR: δ 8.36 (dd, J = 8.0 and J = 1.6 Hz, 4H), 8.27 (s, 2H), 8.20 (d, J = 8.5 Hz, 2H), 8.11 (d, J = 8.5 Hz, 2H), 7.61-7.49 (m, 6H) and 3.35 (s, 2H). *Anal.* Calcd for $C_{24}H_{18}N_2O$: C, 82.26; H, 5.18; N, 8.00. Found: C, 81.98; H, 5.06; N, 7.83] both at room temperature and on heating (see Text).

corresponding pyridines **2** from pyrylium salts **3** occurs readily, even if the anion is non-nucleophilic especially at elevated temperatures.[28] So, it is important that the aqueous solution of methylamine into pyrylium salt be added slowly at room temperature and then the resulting mixture kept at that temperature in order to minimize formation of pyridines. We found that 4-aryl-2,6-diphenyl-1-methylpyridinium perchlorates can be obtained in a reasonably good yield from 1 equiv of the corresponding pyrylium salts and 50 equiv of methylamine (Table 3). When less amine was used, the products were contaminated by divinylogous amide intermediates.[3]

In conclusion, the simplicity, generality, efficiency and mildness of the proposed method recommend the present procedures for the preparation of compounds **1** as well as for their convertion into **2** and **3**.

EXPERIMENTAL SECTION

All melting points were determined on a hot-stage microscope and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-200 spectrometer in the FT mode operating at 200 MHz for approxi-

mately 0.2 M solutions in DMSO-d_6. TMS was used as an internal standard. Known products were identified by the comparison of their melting points and NMR spectra with those of authentic samples available in the literature. For those showing divergent melting points, elemental analyses were carried out. New compounds have been characterized microanalitically and by their ^{1}H NMR spectra. Commercially available acetophenone as well as benzaldehydes were used as received.

TABLE 3. Preparation of 1-Methyl-4-Aryl-2,6-Diphenylpyridinium Perchlorates (**3**)

Compd No.	Yield (%)	mp (°C)	lit. mp. (°C)	Solvent for cryst.	Time (min)
3a	85	196-198	215,[3] 216,[25] 213-215[24]	EtOH	10
3b	59	213-214	–	MeOH	15
3c	54	235-257[a]	238,[12] 262-3[27]	AcOH	10
3d	67	206-211[b]	–	MeOH	15
3e	76	240-242	–	MeOH	15
3f	71	266.5-268	–	MeOH	15
3g	91	148-153[b]	–	H_2O-MeOH (1:1)	15
3h	66	227-228.5	–	MeOH	15
3i	64	249-251	–	MeOH	15
3j	67	221.5-222	–	MeOH	10
3k	25	268.5-269.5	–	H_2O-MeOH (2:1)	10
3l	40	219-220	–	MeOH	30
3n	35	203-203.5	–	MeOH	30

a) Resolidification and repeated fusion at 257° b) Polymorphic changes can be seen in the given temperature range.

4-Aryl-2,6-diphenylpyrylium Perchlorates (1). General Procedures. Method A.- A mixture of the corresponding benzaldehyde (0.02 mol), acetophenone (0.04 mol) and conc. sulfuric acid (d = 1.82, 10 mL, 0.18 mol) was heated at 100° for the time given in Table 1. The reaction mixture cooled to room temperature was poured into ethanol (150 mL), the resulting solution treated (CAUTION: perchloric acid is explosive) with 70% perchloric acid (1.6 mL, 0.02 mol) and allowed to stand overnight in refrigerator. The precipitated crystals were collected, washed with ethyl ether and recrystallized (Table 1).

Method B.- A mixture of the benzaldehyde (0.02 mol), acetophenone (0.04 mol) and 70% perchloric acid (3.2 mL, 0.04 mol) in toluene (25 mL) was refluxed for the specified amount of time (Table 1). The cold (10°) reaction mixture was poured carefully into ethyl ether (200 mL). Crude crystals of **1** were formed after standing overnight in refrigerator. For further details see Method A and Table 1.

4-Aryl-2,6-diphenylpyridines (2). General Procedure.- To a stirred solution of the corresponding pyrylium perchlorate (0.01 mol) in acetone (40 mL) 25% aqueous solution of ammonia (37.5 mL, 0.5 mol) was added dropwise for 10 min at 50°. The reaction mixture was stirred and heated at the same

temperature for the specified amount of time (Table 2). Then water (150 mL) was added, the resulting solid was collected and purified by recrystallization (Table 2).

TABLE 4. ^{1}H NMR and Elemental Analyses of Compounds **1-3**

Cmpd	Elemental Analyses (Found)			^{1}H NMR (δ, ppm; J, Hz)
	C	H	N	
1a	67.58 (67.81)	4.19 (4.33)		
1b	68.17 (68.25)	4.53 (4.44)		
1d	65.68 (65.84)	4.36 (4.57)		
1e	63.36 (63.21)	4.21 (4.19)		9.10 (s, 2H), 8.61 (d, J = 8.8 Hz, 2H), 8.54 (dd, J = 8.3 and J = 1.7 Hz, 4H), 7.86-7.74 (m, 6H), 7.62(d, J = 8.8 Hz, 2H) and 2.68 (s,3H)
1f	60.45 (60.57)	3.38 (3.21)		9.26 (s, 2H), 8.75 (d, J = 8.4 Hz, 2H), 8.62 (dd, J = 8.1 Hz and J = 1.4 Hz, 4H), 8.17 (d, J = 8.4 Hz, 2H) and 7.90-7.77 (m, 6H)
1g	64.72 (64.94)	3.78 (3.85)		
1h	62.32 (62.09)	3.64 (3.58)		
1i	56.64 (56.79)	3.31 (3.22)		
1k	64.31 (64.55)	4.10 (4.01)		9.22 (s, 2H), 8.67 (d, J = 8.6 Hz, 2H), 8.61-8.57 (m, 6H), 8.25 (d, J = 8.6 Hz, 2H), 7.89-7.77 (m, 6H) and 3.96 (s, 3H)
1l	62.32 (62.50)	3.64 (3.53)		
1m	60.87 (61.02)	3.55 (3.70)	3.09 (2.94)	
2c	85.68 (85.51)	6.33 (6.20)	7.99 (8.17)	
2e	81.55 (81.74)	5.42 (5.64)	3.96 (3.82)	8.44-8.41 (m, 4H), 8.27 (s, 2H), 8.10 (d, J = 8.4 Hz, 2H), 7.68-7.58 (m, 6H), 7.52 (d, J = 8.4 Hz, 2H) and 2.65 (s, 3H)
2f	76.79 (76.97)	4.29 (4.08)	3.73 (3.61)	8.37-8.31 (m, 2H), 8.35 (d, J = 8.3 Hz, 2H), 8.27 (s, 2H), 7.93 (d, J = 8.3 Hz, 2H) and 7.60-7.50 (m, 6H)

Table 4. (Cont'd)

2k	82.17 (82.00)	5.24 (5.46)	3.83 (3.61)	8.44 (dd, J = 8.2 and J = 1.3 Hz, 4H), 8.36 (s, 2H), 8.31 (d, J = 8.5 Hz, 2H), 8.22 (d, J = 8.5 Hz, 2H), 7.69-7.57 (m, 6H) and 4.01 (s, 3H)
2l	80.81 (81.02)	4.72 (4.90)	4.10 (3.92)	8.45 (dd, J = 8.5 and J = 1.6 Hz, 4H), 8.33 (s, 2H), 8.30-8.28 (m, 1H), 8.14-8.12 (m, 1H) and 7.69-7.61 (m, 8H)
3a	68.33 (68.53)	4.78 (4.99)	3.32 (3.24)	
3b	68.88 (69.02)	5.09 (4.95)	3.21 (3.17)	8.53 (s, 2H), 8.19 (d, J = 8.2 Hz, 2H), 7.98-7.95 (m, 4H), 7.82-7.80 (m, 6H), 7.53 (d, J = 8.2 Hz, 2H), 3.85 (s, 3H) and 2.52 (s, 3H)
3c	67.16 (67.03)	5.42 (5.24)	6.03 (5.87)	
3d	66.43 (66.58)	4.91 (4.99)	3.10 (3.15)	8.49 (s, 2H), 8.39 (d, J = 8.9 Hz, 2H), 7.97-7.94 (m, 4H), 7.81-7.79 (m, 6H), 7.25 (d, J = 8.9 Hz, 2H), 3.82 (s, 3H) and 3.98 (s, 3H)
3e	64.15 (64.36)	4.74 (4.50)	2.99 (3.11)	8.53 (s, 2H), 8.33 (d, J = 8.7 Hz, 2H), 7.98-7.95 (m, 4H), 7.82-7.79 (m, 6H), 7.55 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H) and 2.63 (s, 3H)
3f	61.29 (61.52)	3.91 (4.10)	2.86 (3.08)	8.56 (s, 2H), 8.48 (d, J = 8.2 Hz, 2H), 7.99 (d, J = 8.2 Hz, 2H), 7.92-7.86 (m, 4H), 7.76-7.69 (m, 6H) and 3.82 (s, 3H)
3g	65.53 (65.70)	4.35 (4.52)	3.18 (3.13)	8.47 (s, 2H), 8.46-8.34 (m, 2H), 7.89-7.84 (m, 4H), 7.73-7.68 (m, 6H), 7.52-7.43 (m, 2H) and 3.77 (s, 3H)
3h	63.17 (63.33)	4.20 (3.97)	3.10 (3.32)	8.59 (s, 2H), 8.41 (d, J = 8.7 Hz, 2H), 7.98-7.96 (m, 4H), 7.79-7.82 (m, 6H), 7.79 (d, J = 8.7 Hz, 2H) and 3.88 (s, 3H)
3i	57.56 (57.38)	3.82 (4.05)	2.80 (3.01)	8.58 (s, 2H), 8.33 (d, J = 8.7 Hz, 2H), 7.99-7.96 (m, 4H), 7.82-7.80 (m, 6H), 7.93 (d, J = 8.7 Hz, 2H) and 3.88 (s, 3H)
3j	61.74 (61.80)	4.10 (3.90)	6.00 (5.78)	8.69 (s, 2H), 8.63 (d, J = 9.0 Hz, 2H), 8.52 (d, J = 9.0 Hz, 2H), 8.00-7.97 (m, 4H), 7.83-7.80 (m, 6H) and 3.93 (s, 3H)
3k	65.07 (65.26)	4.62 (4.77)	2.92 (2.79)	8.54 (s, 2H), 8.41 (d, J = 8.6 Hz, 2H), 8.14 (d, J = 8.6 Hz, 2H), 7.91-7.86 (m, 4H), 7.74-7.69 (m, 6H), 3.91 (s, 3H) and 3.81 (s, 3H)
3l	63.17 (63.00)	4.20 (4.05)	3.10 (2.94)	8.63 (s, 2H), 8.53-8.52 (m, 1H), 8.35-8.32 (m, 1H), 7.99-7.95 (m, 4H), 7.82-7.80 (m, 6H), 7.79-7.71 (m, 2H) and 3.90 (s, 3H)
3n	63.17 (63.05)	4.20 (4.42)	3.10 (2.98)	8.40 (s, 2H), 8.01-7.97 (m, 4H), 7.94-7.85 (m, 1H), 7.82-7.79 (m, 6H), 7.75-7.69 (m, 3H) and 3.96 (s, 3H)

1-Methyl-4-aryl-2,6-diphenylpyridinium Perchlorates (3).- To a stirred solution of the corresponding pyrylium perchlorate (0.01 mol) in acetone 40 mL) 40% aqueous solution of methylamine (43 mL, 0.5 mol) was added dropwise for 10 min at room temperature. Stirring was continued for the time shown in Table 3. Then water (150 mL) was added, the resulting crude pyridinium perchlorate was collected, washed with ethyl ether and recrystallized (Table 3).

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