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Efficient Synthesis of 2,6-Diphenyl-4-arylpyrylium Tetrafluoroborate

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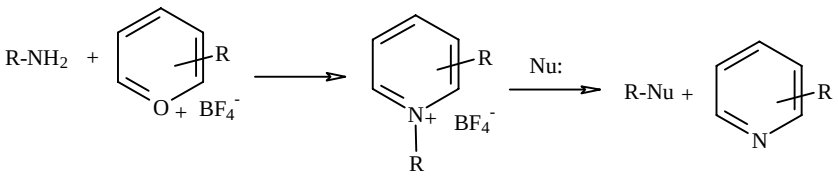
Abstract: Four pyrylium salts, (2,6-diphenyl-4-arylpyrylium tetrafluoroborate, aryl = C_6H_5, 4-MeO C_6H_4, 4-$Me_2NC_6H_4$, 4-$NO_2C_6H_4$) were synthesized efficiently and economically from acetophenone and substituted chalcones in the presence of borontrifluoride.

Keywords: 2,6-Diphenyl-4-arylpyrylium tetrafluoroborate, chalcone, acetophenone, borontrifuoride.

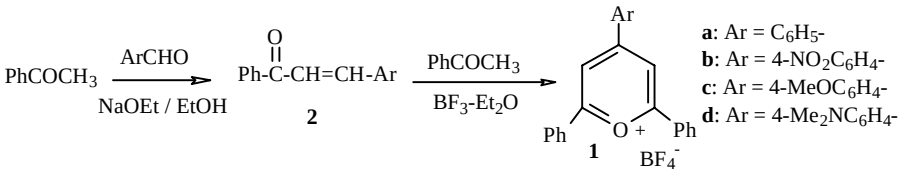
Pyrylium salts are powerful reagents for converting primary amines to N-substituted pyridinium salts[1] and which can be transformed to various organic compounds by reactions with nucleophiles[2] (**Scheme 1**).

Scheme 1



The cost of pyrylium salt, however, restricted its application in organic synthesis. In this manuscript, we reported efficient and economic synthesis of 2,6-diphenyl-4-arylpyrylium tetrafluoroborate **1a-d** using acetophenone and substituted chalcones as starting materials (**Scheme 2**).

Scheme 2



Chalcones **2a-d** were prepared from the reactions of acetophenone and substituted benzaldehydes with sodium ethoxide in ethanol at room temperature for 3 hours. Benzaldehyde containing electron withdrawing substituent gave higher yields (**Table**

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1). Product **2a-d** were recrystallized from ethanol/water to form needle crystals with white,
light brown, and orange color, respectively.

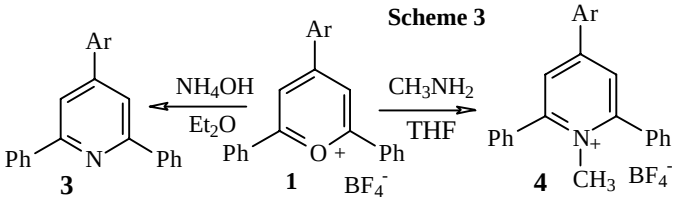
Table 1 The yields and melting points of compounds **1a-d** and **2a-d**

Compd	1a	1b	1c	1d	2a	2b	2c	2d
Yield (%)	65.4	68.2	47.8	36.4	85.2	90.1	75.4	70.2
mp (°C)	205-1	109-11	218-20	106-8	55-57	115-7	75-77	165-7

The pyrylium salts **1a-d** were synthesized by treatment of the corresponding chalcones **2a-d** with acetophenone (1:1 eq.) in excess of BF_3-Et_2O (47 %) solution, which functioning as Lewis acid and solvent, stirred 1 hour at 80°C. Then the mixtures were treated with aqueous HBF_4 (10 %). Products **1a-d** (yielded 65, 68, 48 and 36 %, respectively) appeared as yellow, orange-yellow, brown, and purple powder.

In order to confirm the structures, pyrylium salt **1** were converted to the analogous pyridine **3a**, **3d** and pryidinium salts **4b**, **4c** by treatment with aqueous ammonia in ether or methylamine in THF at room temperature for 2 hours[1] (**Scheme 3**). After removal of solvents and washed with water, **3** and **4** were formed as yellow powder in high yields (all > 90 %). The structures of products were identified by NMR (^1H, ^{13}C DEPT) spectra[4].

Scheme 3



a: Ar = C_6H_5-
b: Ar = 4-$NO_2C_6H_4$-
c: Ar = 4-$MeOC_6H_4$-
d: Ar = 4-$Me_2NC_6H_4$-

In summary, it was demonstrated in this work that 2,6-diphenyl-4-arylpyrylium tetrafluoroborates (Ar = H, NO_2, MeO, Me_2N) **1a-d** could be synthesized in large scale and economically using benzaldehyde and acetophenone as the starting materials.

References and Notes

1. A. L. Katritzky, ; O. Rubio, *J. Org. Chem.*, **1984**, *49*, 448.
2. A. J. Boulton, J. Epsztajn, A. L. Katritzky, P. L. Nie, *Tetrahedron Lett*., **1976**, 2689.
3. A. R. Ketritzky, R. Awartani, R. C. Patel, *J. Org. Chem.*, **1982**, *47*, 498.
4. NMR spectral data (200 MHz for ^1H NMR and 50 MHz for ^{13}C NMR, in $CDCl_3$, δppm) of compound **2a**: ^1H NMR: 7.38-7.77 (m, 10H), 8.01 (d, 2H, J = 8.4 Hz, Ph). Compound **2b**: ^1H NMR: 7.53-7.82 (s, 7H), 8.05 (d, 2H, J = 7.8 Hz, Ph), 8.28 (d, 2H, J = 8.2 Hz, Ph). Compound **2c**: ^1H NMR: 3.82 (s, 3H, OCH_3), 6.90 (d, 2H, J = 8.6 Hz, Ph), 7.35-7.72 (m, 7H), 7.98 (d, 2H, J = 8.4 Hz, Ph). Compound **2d**: ^1H NMR: 2.98 (s, 6H, NMe_2), 6.64 (d, 2H, J = 8.4 Hz, Ph), 7.32-7.80 (m, 7H), 8.01 (d, 2H, J = 8.6 Hz, Ph). Compound **1a**: ^{13}C NMR (in DMF): 113.63, 126.43, 126.53, 126.91, 127.13, 127.58, 128.20, 131.10, 133.36, 164.18, 168.96. Compound **1d**: ^{13}C NMR (in DMF): 38.93 (NMe_2), 112.05, 116.10, 123.54, 126.43, 126.80, 128.78, 130.71, 136.77, 142.66, 148.77, 187.11. Compound **3a**: ^1H NMR: 7.43-7.47 (m, 8H), 7.66 (m, 3H), 7.82 (s, 2H), 8.15 (d, 4H, J = 8.6 Hz). Compound **3d**: ^1H NMR: 3.03 (s, 6H, NMe_2), 6.68 (d, 2H, J = 9.2 Hz), 7.30-7.78 (m, 14H), 8.00 (d, 4H, J = 8.2 Hz). ^{13}C NMR: 40.07 (NMe_2), 111.79, 116.90, 122.61, 128.27, 128.40, 130.37, 132.09, 139.06, 145.82, 152.01, 190.65. Compound **4b**: ^1H NMR: 3.92 (s, 3H, CH_3), 7.61 (m, 6H), 7.80-7.98 (m, 8H), 8.32 (d, 2H, J = 9.0 Hz, Ph). Compound **4c**: ^1H NMR: 3.86 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 7.02 (d, 2H, J = 9.2 Hz), 7.61 (m, 6H), 7.80-7.84 (m, 8H). ^{13}C NMR:

44.60 (CH_3), 55.64 (OCH_3), 115.31, 124.55, 125.84, 129.18, 129.44, 129.77, 131.14, 132.94, 154.96, 156.88, 163.24.

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