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# Synthesis of 2,6-Disubstituted Fluorenones

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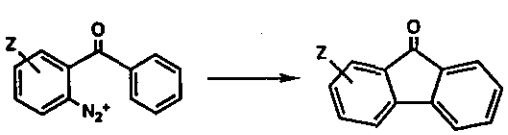
Various 2,6-disubstituted fluorenones **1a-1g** were synthesized by the dry salt decomposition of 5,4′-disubstituted 2-diazoniobenzophenone tetrafluoroborates **8a-8g** via Pschorr cyclization in reasonable yields.

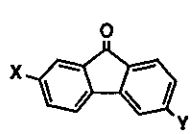
## INTRODUCTION

Fluorenones and their derivatives have been known to be good antiviral agents[1] and potential ligands for metal $\pi$-complexes.[2] Various preparations of fluorenones have been achieved.[3a-3i] These include (1) the conversion of *p*-substituted benzoic anhydrides into the corresponding fluorenones by using Wilkinson catalyst,[3a] (2) the Diels-Alder reaction of sorbic acid with substituted styrenes, followed by the Friedel-Crafts type acylation,[3c] (3) the direct nitration of fluorenones, and accompanied by a subsequent transformation of the nitro group into other functions, (4) the oxidation of fluoranthene,[3g] and (5) the Pschorr cyclization of 2-diazoniobenzophenones. Among these, the most fruitful ought to be the Pschorr cyclization (Eq. 1) which allows one to obtain various substituted fluorenones. Recently, Kyba et al. demonstrated a photochemically induced Pschorr cyclization to prepare variously substituted azafluorenones and fluorenones.[4]



(1)

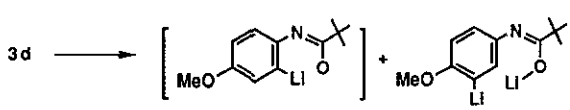
Here, we would like to show our efforts in the study of the dry salt decomposition of a series of 5,4′-disubstituted 2-diazoniobenzophenones leading to the 2,6-disubstituted fluorenones **1a-1g**.




| | | |
|---|---|---|
| **1 a** | X = Me | Y = Me |
| **b** | Cl | OMe |
| **c** | Me | Cl |
| **d** | Cl | Me |
| **e** | F | OMe |
| **f** | F | F |
| **g** | OMe | F |

## RESULTS AND DISCUSSION

Similar to the synthetic approach developed by Kyba and co-workers,[4] the preparative route to the 2,6-di-substituted fluorenones **1** is outlined in Scheme I. By using the conventional Schotten-Bauman method,[5] in which pyridine was used as a base to trap hydrogen chloride, the pivalamides **3** were obtained from the corresponding anilines **2** in greater than 90 % yields. According to the procedure of Fuhrer and Gschwend,[6] lithiation of **3** in tetrahydrofuran underwent quite well, except **3d** in which the substituent was the methoxyl group. This was probably due to the competitive lithiation directed by the pivalamido group and the methoxyl group (Eq. 2).[6] The addition of aldehydes **4** to anions **10** produced the desired alcohols **5**, and a subsequent oxidation of such alcohols by pyridinium chlorochromate (PCC) yielded the corresponding ketones **6**. With the temperature controlled in the range of 80 to 95°C, the acid-catalyzed hydrolysis of the ketoamides **6** gave the ketoamines **7** quantitatively. It is noteworthy to mention that an inverse base quench in the workup step avoids the generation of imines.[4]

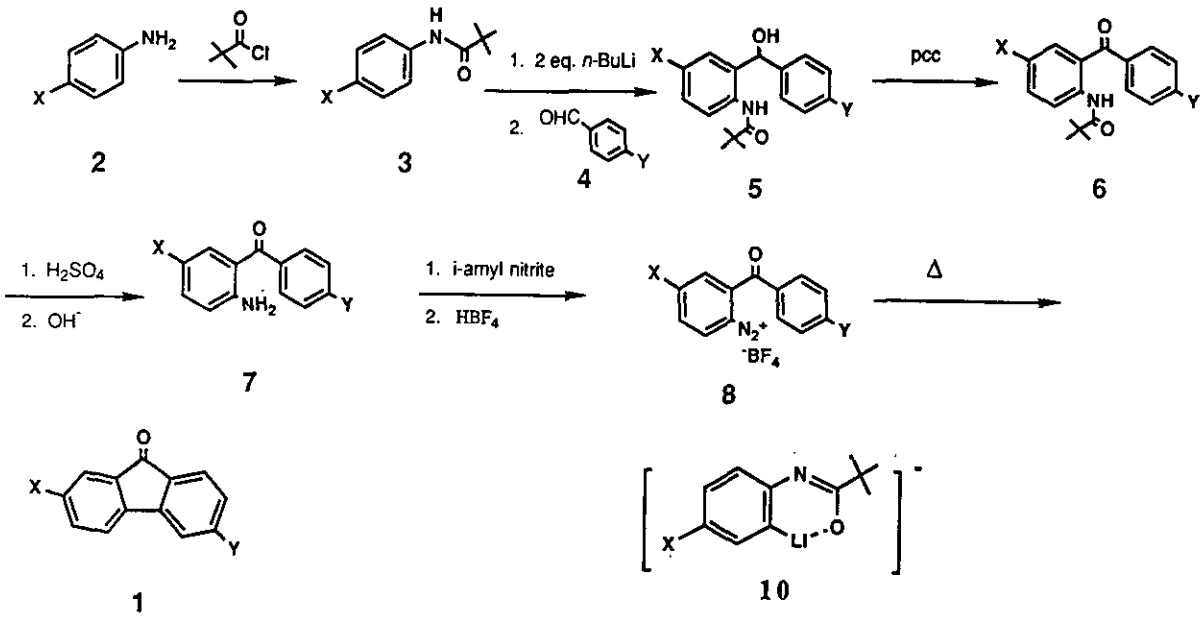


(2)

With the ketoamines **7a-7g** in hand, several reaction conditions for the Pschorr cyclization to produce the desired fluorenones have been surveyed and the results are listed in Table 1: (1) The diazotization of **7b** in concentrated sulfuric acid, followed by a thermal decomposition was conducted at 50°C, and the fluorenone **1b** was obtained in poor yield. Nevertheless, such a conventional reaction condition has been used to produce fluorenones in good yields.[3h,3i] (2) With $[Ru(bipy)_3]Cl_2$ as a homogeneous catalyst to induce the cyclization photochemically,[4,13] the

Dedicated to Professor Yau-Tang Lin (林耀堂) on the occasion of his eightieth birthday.

**Scheme I** The synthetic route to **1a-1g**[a]



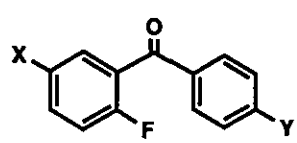

[a] The substitutents of X and Y are given according to the corresponding assignment in **1**.

diazonium salt of **7b** in the diluted acid solution gave no desired product. (3) A heterogenerous catalyst such as $Cu_2O$ used to accelerate the cyclization[7] of the diazonium tetrafluoroborate **8b** resulted in a mixture of the reduction species **11** and **1b** (Eq. 3); however the purification of fluorenone from the mixture turned out to be difficult, even using chromatography. (4) The introduction of sodium iodide to catalyze the Pschorr cyclization[8] for **8d** in acetone gave a mixture of un-cyclized products as identified by the infrared spectroscopy (see below). (5) Instead of in aqueous solution, the thermal decomposition of the diazonium tetrafluoroborate **8c** in benzene solution[9] gave a mixture of **9c** and **1c** in a ratio of 1:1. (6) Finally, the decomposition of the tetrafluoroborate salt of diazonium compounds **8b** in the absence of solvent at a higher temperature,[9] typically around 120°C, appeared to produce more effectively the fluorenone product **1b** along with the fluorinated product **9b** in the ratio of 3:1, favoring the cyclized product.

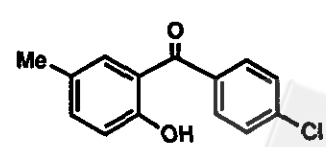
Table 1. Results for The Pschorr Cyclization of Amine **7** under various conditions

| Amine | Diazotization | Reaction Conditions for Pschorr Cyclization | Results | References |
|---|---|---|---|---|
| **7b** | a | 50°C, in conc. $H_2SO_4$ solution | **1b** in low yield | 3h, 3i |
| **7b** | a | catalyst $[Ru(bipy)_3]Cl_2$ in 1 M $H_2SO_4$ at rt | No desired product | 4 |
| **7b** | b | catalyst $Cu_2O$ in 1 M $H_2SO_4$ at rt | **1b:11 (1:1) in low yield** | 7 |
| **7d** | b | catalyst NaI in acetone solution at rt | No desired product | 8 |
| **7c** | b | in 0.1 M $H_2SO_4$ at 60°C | **1c** (15%) + **13** (10%) | 11, 12 |
| **7c** | b | refluxing benzene solution | **1c** (30%) + **9c** (30%) | 9 |
| **7b** | b | dry salt decomposition at raising temperature | **1b** (61%) + **9b** (20%) | 9 |
| **7c** | b | dry salt decomposition at raising temperature | **1c** (28%) + **9c** (19%) | 9 |

[a] $NaNO_2$/conc. $H_2SO_4$ in ice-bath [b] (i) isoamyl nitrite (ii) $HBF_4$/MeOH in ice-bath



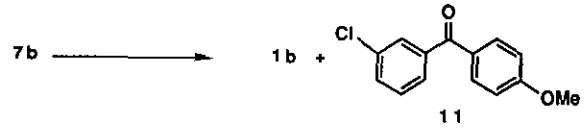
**9b** X = Cl, Y = OMe
**9c** X = Me, Y = Cl



**13**

Table 2. The Physical, Spectroscopic Data and Elemental Analysis of Compounds **1a-1g**

| Compound (Yield) | mp(°C) | IR ($\upsilon_{C=O}$,cm$^{-1}$) | $^1$H NMR | Anal. Calcd C | Calcd H | Found C | Found H |
|---|---|---|---|---|---|---|---|
| **1a** (57%) | 78-80 | 1709 | 7.51 (*d*, J = 7Hz, 1H), 7.44-7.43 (*m*, 1H), 7.35 (*d*, J = 7Hz, 1H), 7.26 (*s*, 1H), 7.25-7.22 (*m*, 1H), 7.05-7.01 (*m*, 1H), 2.40 (*s*, 3H), 2.36 (*s*, 3H) | 86.51 for $C_{15}H_{12}O$ | 5.81 | 86.12 | 5.57 |
| **1b** (61%) | 142-143 | 1711 | 7.63 (*d*, J = 8Hz, 1H), 7.59-7.57 (*m*, 1H), 7.42-7.41 (*m*, 2H), 7.00 (*d*, J = 2Hz, 1H), 6.76 (*dd*, J = 8, 2Hz, 1H), 3.92 (*s*, 3H) | 68.73 for $C_{14}H_9ClO_2$ | 3.71 | 68.38 | 3.53 |
| **1c** (47%) | 146 | 1721 | 7.53 (*d*, J = 8Hz, 1H), 7.46 (*s*, 1H), 7.42 (*d*, J = 2Hz, 1H), 7.36 (*d*, J = 7Hz, 1H), 7.28 (*d*, J = 8Hz, 1H), 7.21 (*dd*, J = 8, 2Hz, 1H), 2.37 (*s*, 3H) | 73.53 for $C_{14}H_9OCl$ | 3.97 | 73.60 | 3.76 |
| **1d** (45%) | 106-107 | 1717 | 7.58-7.57 (*m*, 1H), 7.55 (*d*, J = 7Hz, 1H), 7.42 (*s*, 1H), 7.41 (*s*, 1H), 7.30 (*s*, 1H), 7.09 (*d*, J = 7Hz, 1H), 2.43 (*s*, 3H) | 73.53 for $C_{14}H_9OCl$ | 3.97 | 73.60 | 3.8 |
| **1e** (60%) | 128-129 | 1710 | 7.62 (*d*, J = 8Hz, 1H), 7.41 (*dd*, J = 9, 8Hz, 1H), 7.31 (*dd*, J = 8, 2Hz, 1H), 7.18-7.08 (*m*, 1H), 6.98 (*d*, J = 2Hz, 1H), 6.73 (*dd*, J = 8, 2 Hz, 1H) | 73.68 for $C_{14}H_9O_2F$ | 3.97 | 73.47 | 3.80 |
| **1f** (45%) | 178-179 | 1721 | 7.66 (*dd*, J = 8, 5Hz, 1H), 7.46 (*dd*, J = 8, 4Hz, 1H), 7.35 (*dd*, J = 7, 2Hz, 1H), 7.19-7.14 (*m*, 2H), 6.99-6.90 (*m*, 1H) | 72.23 for $C_{13}H_6F_2O$ | 2.80 | 72.08 | 2.61 |
| **1g** (54%) | 139-140 | 1719 | 7.59 (*dd*, J = 8, 5Hz, 1H), 7.38 (*d*, J = 8Hz, 1H), 7.20 (*d*, J = 2Hz, 1H), 7.08 (*dd*, J = 8, 2Hz, 1H), 7.01 (*dd*, J = 6, 2Hz, 1H), 6.85-6.84 (*m*, 1H), 3.87 (*d*, J = 1Hz, 3H) | 73.68 for $C_{14}H_9O_2F$ | 3.97 | 73.48 | 3.99 |



(3)

The preparations of the 2,6-disubstituted fluorenones **1a-1g** were all accomplished by direct thermal decomposition of the diazonium salt and no regio-isomer was obtained simply due to the symmetry of aromatic ring in the cyclization step. The fluorenones **1** were obtained in pure form by recrystallization from methanol solution and were all isolated as yellow crystalline solids in reasonable yields. The identification of **1** by spectroscopic methods and elemental analysis was straightforward (Table 2). Both the cyclized and the fluorinated products are readily identifiable by their infrared absorptions. The stretching vibration of carbonyl groups in the substituted benzophenones **9** (below 1700 cm$^{-1}$) has a lower wavenumber than those of fluorenones **1** (1709-1721 cm$^{-1}$).

This work presents synthetic information for the variously 2,6-disubstituted fluorenones, but the results seem to contribute no conclusion about the mechanistic argument of the Pschorr cyclization.[7,9,10] Our research on the coordination behavior of this series of fluorenones toward metals is currently in progress.

## EXPERIMENTAL SECTION

### General Information

Infrared spectra of samples were recorded on a Perkin-Elmer 983 grating spectrophotometer in $CH_2Cl_2$ solution, unless otherwise stated. Proton magnetic resonance spectra were obtained in $CDCl_3$ on either a Bruker AC200 or an Varian EM-390 spectrometer. Chemical shifts are given in parts per million relative to tetramethylsilane. Melting points were determined by using a Mel-Temp II capillary melting point apparatus, and are uncorrected.

All solutions were dried over anhydrous magnesium sulfate. All concentration of solutions were carried out on a rotary evaporator under water aspirator pressures.

Tetrahydrofuran was distilled under nitrogen from benzophenone ketyl. *N*-pivaloyl-*p*-toluidine **3a**,[6] *N*-pivaloyl-*p*-chloroaniline **3b**,[6] *N*-pivaloyl-*p*-fluoroaniline **3c**,[6] and *N*-pivaloyl-*p*-anisidine **3d**[4] were prepared according the reported methods.

### *N*-Pivaloyl-*p*-toluidine (3a)

Into a flask fitted with an addition funnel and a refluxing condenser was placed *p*-toluidine (3.0 g, 28 mmol) and pyridine (2.3 mL, 28 mmol) in $CHCl_3$(20 mL). Pivaloyl chloride (3.6 mL, 28 mmol) was added dropwise through the addition funnel to the above solution. The resulting

mixture was stirred and heated under reflux overnight. After being cooled to room temperature, the solution was washed with water (4 x 50 mL) and brine and dried. After removal of solvents, a white solid was obtained. Recrystallization from methanol gave the desired compound as a colorless crystal (5.0 g, 92 %): mp 119-121°C, which was essentially identical as described in the literature.[6]

**2-Pivalamido-5-methyl-4′-methylbenzophenone (6a)**

To a solution of *N*-pivaloyl toluidine **3a** (5.0 g, 26 mmol) in THF (40 mL), a 1.6 M hexane solution of *n*-BuLi (40.8 mL, 65 mmol) was added dropwise at ice-bath temperature under nitrogen atmosphere. After stirring overnight, a large quantity of white solid appeared. 4-Methylbenzaldehyde (4.6 mL, 40 mmol) was added dropwise to the above anion solution at -10°C and the white solid disappeared immediately. The resulting red color solution was allowed to warm to room temperature and stirred overnight again. Ethyl acetate (5 mL) was added to quench the reaction. This mixture was poured into a mixture of water (50 mL) and ether, and the ethereal extract was washed with brine and dried. Instead of direct isolation of **5a**, the crude reaction mixture was dissolved in dry methylene chloride (50 mL), and pyridinium chlorochromate (8.45 g, 40 mmol) was added. The suspension was stirred at room temperature ovemight. The reaction mixture was diluted with ether (50 mL) and filtered through a column of basic alumina (100 g). The filtrate was concentrated to give a green oil. Addition of methanol gave palegreen crystals. This crystal was identified as the desired ketone **6a** (6.9 g, 67%).

2-Pivalamido-5-chloro-4′-methoxybenzophenone (**6b**), 2-pivalamido-5-methyl-4′-chlorobenzophenone (**6c**), 2-pivalamido-5-chloro-4′-methylbenzophenone (**6d**), 2-pivalamido-5-fluoro-4′-methoxybenzophenone (**6e**), 2-pivalamido-5-fluoro-4′-fluorobenzophenone (**6f**) and 2-pivalamido-5-methoxy-4′-fluorobenzophenone (**6g**) were prepared by a method similar to that for **6a**, and their physical and spectral data are listed in Table 3.

**2-Amino-5-methyl-4′-methylbenzophenone (7a)**

A suspension of compound **6a** (5.0g, 16 mmol) in a 70 % solution of sulfuric acid (100 mL) was heated to the temperature range of 80 - 95°C overnight. After being cooled to room temperature, the solution was diluted with water (100 mL) and cooled further to 0°C. Ice-cooled NaOH solution was added to make the solution basic, and the solution was extracted with methylene chloride (4 x 50 mL). The organic extracts were washed with water and brine and dried. The yellow solution was concentrated to give pure **7a** as a yellow solid (3.6 g, 98 %), and this material was pure enough for analysis.

Table 3. The Yields, Physical and Spectroscopic Data for Compounds **6a-6g**

| Compound | Yield(%) | mp (°C) | IR ($cm^{-1}$) | $^1H$ NMR |
|---|---|---|---|---|
| **6a** | 67 | 103-104 | 3321 | 10.96 (*br*, 1 H), 8.53 (*d*, J = 10 Hz, 1 H), |
| | | | 1674 | 7.62 (*d*, J = 8 Hz, 2 H), 7.45-7.20 (*m*, 4 H), |
| | | | 1627 | 2.45 (*s*, 3 H), 2.29 (*s*, 3 H), 1.33 (*s*, 9 H) |
| **6b** | 66 | 97-98 | 3336 | 10.78 (*br*, 1 H), 8.60 (*d*, J = 10 Hz, 1 H), |
| | | | 1680 | 7.71 (*dd*, J = 7, 2 Hz, 2 H), 7.50-7.43 (*m*, 2 H), |
| | | | 1632 | 6.97 (*dd*, J = 7, 2 Hz, 2 H), 3.89 (*s*, 3 H), 1.30 (*s*, 3 H) |
| **6c** | 50 | 104 | 3331 | 10.94 (*br*, 1 H), 8.55 (*d*, J = 9 Hz, 1 H) |
| | | | 1675 | 7.62 (*d*, J = 8 Hz, 2 H), 7.50-7.20 (*m*, 4 H), |
| | | | 1630 | 2.27 (*s*, 3 H), 1.31 (*s*, 9 H) |
| **6d** | 70 | 116.5-117.5 | 3331 | 10.96 (*br*, 1 H), 8.70-8.60 (*m*, 1 H), |
| | | | 1681 | 7.63-7.57 (*m*, 2 H), 7.33-7.24 (*m*, 2 H), |
| | | | 1637 | 2.43 (*s*, 3 H), 1.30 (*s*, 9 H) |
| **6e** | 57 | 102 | 3338 | 10.90 (*br*, 1 H), 8.73-8.44 (*m*, 1 H), |
| | | | 1674 | 7.82-7.65 (*m*, 2 H), 7.35-7.10 (*m*, 2 H), |
| | | | 1632 | 7.04-6.83 (*m*, 2 H), 3.83 (*s*, 3 H), 1.30 (*s*, 9 H) |
| **6f** | 61 | not available | 3343 | 10.83 (*br*, 1 H), 8.70-8.53 (*m*, 1 H), |
| | | | 1680 | 7.80-7.66 (*m*, 2 H), 7.36-7.10 (*m*, 4 H), |
| | | | 1641 | 1.31 (*s*, 9 H) |
| **6g** | 24 | 87.5-88 | 3349 | 10.61 (*br*, 1 H), 8.55 (*d*, J = 9 Hz, 1 H), |
| | | | 1677 | 7.83-7.72 (*m*, 2 H), 7.30-7.10 (*m*, 3 H), |
| | | | 1640 | 7.04-6.98 (*m*, 1 H), 3.76 (*s*, 3 H), 1.32 (*s*, 9 H) |

Table 4. The Yields, Melting Points, $^1$H NMR Data and Elemental Analyses for **7a-7g**

| Compound | Yield(%) | mp (°C) | IR ($cm^{-1}$) | $^1$H NMR | Anal. Calcd C H N | Found C H N |
|---|---|---|---|---|---|---|
| **7a** | 98 | 87 | 3485<br>3360<br>1626 | 7.53 (*d*, J = 7 Hz, 2 H), 7.90-6.85 (*m*, 3 H), 6.42 (*d*, J = 7 Hz, 2 H), 5.73 (*br*, 2 H), 2.40 (*s*, 3 H) | 79.97 6.71 6.22 for $C_{15}H_{15}NO$ | 80.11 6.53 6.21 |
| **7b** | 97 | 90 | 3488<br>3365<br>1627 | 7.57 (*d*, J = 9 Hz, 2 H), 7.30 (*d*, J = 3 Hz, 1 H), 7.20 (*dd*, J = 9,3 Hz, 1 H), 6.85 (*d*, J = 9Hz, 2 H), 6.55 (*d*, J = 9Hz, 1 H), 5.82 (*br*, 2 H), 3.72 (*s*, 3 H) | 64.25 4.62 5.35 for $C_{14}H_{12}ClNO_2$ | 64.28 4.50 5.02 |
| **7c** | 93 | 90-91 | 3494<br>3358<br>1625 | 7.55 (*d*, J = 9 Hz, 2 H), 7.37 (*d*, J = 9 Hz, 2 H), 7.15 (*d*, J = 9 Hz, 1 H), 7.04 (*d*, J = 2 Hz, 1 H), 6.60 (*dd*, J = 9, 2 Hz, 1 H), 5.82 (*br*, 2 H), 2.17 (*s*, 3 H) | 68.44 4.92 5.70 for $C_{14}H_{12}ClNO$ | 68.57 4.64 5.57 |
| **7d** | 90 | 102 | 3487<br>3358<br>1629 | 7.61 (*d*, J = 7 Hz, 2 H), 7.50-7.13 (*m*, 3 H), 6.70 (*d*, J = 7 Hz, 2 H), 5.95 (*br*, 2 H), 2.45 (*s*, 3 H) | 68.44 4.92 5.70 for $C_{14}H_{12}ClNO$ | 68.59 4.98 5.62 |
| **7e** | 90 | 68-69 | 3491<br>3363<br>1627 | 7.69 (*dd*, J = 7, 2 Hz, 2 H), 7.16 (*dd*, J = 9, 4 Hz, 1 H), 7.10-7.00 (*m*, 1 H), 6.96 (*dd*, J = 7, 2 Hz, 2 H), 6.69 (*dd*, J = 9, 4 Hz, 1 H), 5.64 (*br*, 2 H), 3.89 (*s*, 3 H) | 68.56 4.93 5.71 for $C_{14}H_{12}FNO_2$ | 68.30 4.69 5.72 |
| **7f** | 99 | 107.5-108.5 | 3489<br>3366<br>1637 | 7.72-7.65 (*m*, 2 H), 7.20-7.03 (*m*, 4 H), 6.74-6.67 (*m*, 1 H), 5.85 (*br*, 2 H) | 66.95 3.89 6.01 for $C_{13}H_9F_2NO$ | 67.00 3.70 5.93 |
| **7g** | 95 | 65-66 | 3484<br>3367<br>1637 | 7.74-7.65 (*m*, 2 H), 7.13-7.09 (*m*, 2 H), 7.01-6.90 (*m*, 2 H), 6.73-6.68 (*d*, J = 9 Hz, 1 H), 5.28 (*br*, 2 H), 3.65 (*s*, 3 H) | 68.56 4.93 5.71 for $C_{14}H_{12}FNO_2$ | 68.43 4.89 5.69 |

2-Amino-5-chloro-4'-methoxybenzophenone (**7b**), 2-amino-5-methyl-4'-chloro-benzophenone (**7c**), 2-amino-5-chloro-4'-methylbenzophenone (**7d**), 2-amino-5-fluoro-4'-methoxybenzophenone (**7e**), 2-amino-5-fluoro-4'-fluorobenzophenone (**7f**) and 2-amino-5-methoxy-4'-fluorobenzophenone (**7g**) were prepared by the method similar to that for **7a**. The physical and spectroscopic data as well as elemental analysis of compounds **7a-7g** are summarized in Table 4.

**2-Diazo-5-methyl-4'-methylbenzophenone tetrafluoroborate (8a)**

The amine **7a** (0.5 g, 1.9 mmol) was dissolved in methanol (20 mL) and a 35% methanol solution of tetrafluoroboric acid (1.2 mL, 5.7 mmol) was added. The resulting orange solution was cooled to 0°C. Isoamyl nitrite (0.26 mL, 2.1 mmol) was added dropwise to the above solution. After stirring for 30 min, ether (50 mL) was added to the reaction mixture and stirred for another 30 min. Upon standing, a white-silver solid was precipitated and was collected (0.47 g, 68%).

According to the procedure described above, 2-diazo-5-chloro-4'-methoxybenzophenone tetrafluoroborate (**8b**), 2-diazo-5-methyl-4'-chlorobenzophenone tetra-fluoroborate (**8c**), 2-diazo-5-chloro-4'-methylbenzophenone tetrafluoroborate (**8d**), 2-diazo-5-fluoro-4'-methoxybenzophenone tetrafluoroborate (**8e**), 2-diazo-5-fluoro-4'-fluorobenzophenone tetrafluoroborate (**8f**) and 2-diazo-5-methoxy-4'-fluorobenzophenone tetrafluoroborate (**8g**) were obtained similarly. Table 5 summarizes the physical and spectroscopic data for **8a-8g**.

Table 5. The Yields Melting Points and Spectroscopic Data of **8a-8g**

| Compound | Yield(%) | mp (°C) | IR ($cm^{-1}$) |
|---|---|---|---|
| **8a** | 68 | 112 | 2267, 1654[a] |
| **8b** | 62 | 113-114 | 2273, 1640[a] |
| **8c** | 55 | 134 | 2275, 1666[b] |
| **8d** | 83 | 138 | 2280, 1664[b] |
| **8e** | 58 | 152 | 2275, 1645[b] |
| **8f** | 92 | 166-167 | 2287, 1674[b] |
| **8g** | 67 | 138-139 | 2251, 1664[b] |

[a] KBr. [b] in $CH_2Cl_2$ solution.

**2,6-Dimethylfluorenone (1a)**

The diazonium salt **8a** (1.0 g, 2.80 mrnol) was placed in a flask fitted with a condenser. The whole system was then evacuated and filled with nitrogen gas. The flask was heated in an oil bath with slow increase of temperature. The temperature was raised to the point at which the decomposition occurred and stayed at that temperature for another 15 min. Normally, decomposition occurred about 120°C and the color of the salt became dark. The reaction mixture was cooled to room temperature and 0.1 N NaOH solution (200 mL) and ether (4 x 50 rnL) were added. The ethereal extract was washed with brine, dried and concentrated to a volume of 5 mL. The residue was chromatographed on a silica gel using benzene as eluent. A yellow solution was collected and concentrated to give yellow solids. Upon recrystallization from methanol, compound **1a** was obtained as a golden yellow crystalline solid (0.4 g, 57%).

2-Chloro-6-methoxyfluorenone (**1b**), 2-methyl-6-chlorofluorenone (**1c**), 2-chloro-6-methylfluorenone (**1d**), 2-fluoro-6-methoxyfluorenone (**1e**), 2,6-difluorofluorenone (**1f**) and 2-methoxy-6-fluorofluorenone (**1g**) were prepared by the method used for **1a**. The melting points, infrared absorptions for carbonyl stretching, $^1$H NMR data as well as elemental analyses of **1a-1g** are summarized in Table 3.

**2-Chloro-6-methoxyfluorenone (1b) and 2-fluoro-5-chloro-4′-methoxybenzophenone (9b)**

The experimental procedure was similar to that for **1a**. Compound **8b** (50 mg, 0.14 rnmol) was placed in a degassed flask fitted with a condenser. The flask was heated in an oil bath to the temperature 120°C and the decomposition occurred. The reaction mixture was cooled to room temperature and 0.1 N NaOH solution (20 mL) and ether (2 x 20 mL) was added. The ethereal extract was washed with brine, dried and concentrated. The residue was chromatographed on silica gel with elution of 5% benzene in hexanes. The first fraction was collected and concentrated to give compound **9b** as a yellow solid (6.7 mg, 20%): IR 1655 ($\nu$C=O) cm$^{-1}$; $^1$H NMR 7.90-7.80 (*m*, 2 H), 7.50-7.37 (*m*, 2 H), 7.28-7.03 (*m*, 1 H), 7.02-6.90 (*m*, 2 H), 3.90 (*s*, 3 H). Whereas the second fraction gave compound **1b** as a yellow solid (20.8 mg, 61 %), and its physical and spectroscopic data were shown in Table 3.

**2-Fluoro-5-methyl-4′-chlorobenzophenone (9c)**

This compound was obtained similarly to that described for **9b** and its spectroscopic data are: IR 1664 ($\nu$C=O) cm$^{-1}$ $^1$H NMR 7.83-7.70 (*m*, 2 H), 7.50-7.38 (*m*, 2 H), 7.37-7.25 (*m*, 2 H), 7.12-6.95(*m*, 1 H), 2.38 (*s*, 3 H).

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**Key Words**

Fluorenone; Synthesis; Thermal decomposition.

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