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Trifluoroacetic Acid: An Efficient Catalyst for Paal-Knorr Pyrrole Synthesis and Its Deprotection

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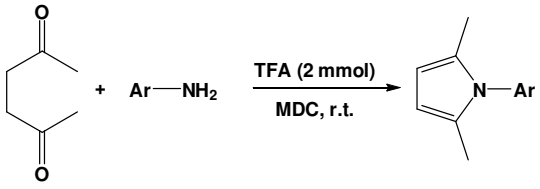
In the present work, we demonstrated a simple and an efficient method for the condensation of substituted aryl/heteroaryl amines with acetonylacetone in the presence of trifluoro acetic acid to afford the corresponding 2,5-dimethyl-1-substitued pyrroles using Paal-Knorr synthesis in excellent yields. Trifluoroacetic acid was used under reflux condition for the deprotection of 2,5-dimethyl-1-substituted pyrroles to their corresponding substituted aryl/heteroaryl amines in moderate yields. 2,5-Dimethyl-1-substitued pyrrole were characterized by NMR and LC-MS. The yield of the compounds was found to be excellent.

Key Words: Deprotection, Amine, Trifluoroacetic acid, Paal-Knorr pyrrole synthesis, Protection, Acetonylacetone.

INTRODUCTION

Pyrrole is a five membered heterocyclic aromatic organic compound and biosynthetic precursor to many natural products[1]. It is widely distributed structural unit in many natural and biologically important molecules such as porphyrins[2], bile pigments[3], co-enzymes[4] and alkaloids[5]. Pyrrole derivatives also display antibacterial[6], antiviral[7], antiinflammatory[8], antioxidant activities[9] and also inhibit cytokine mediated diseases[10-13]. Several procedures have been developed for the synthesis of pyrroles. The well-known methods were Paal-Knorr reaction[14,15], Knorr reaction[16,17] and Hantzsch reaction[18,19]. The Paal-Knorr synthesis involves the condensation of an excess of primary amine with 1-4-dicarbonyl compound and ammonia to provide a pyrrole. The reaction can be performed under neutral or weakly acidic conditions and organic acid such as acetic acid can be added to accelerate the rate of reaction[20].

The synthesis of 2,5-disubstituted pyrroles can be achieved by the classical Paal-Knorr method involving the reaction of 1,4-butanediones with amines. Few methods have been reported for Paal-Knorr synthesis with $Sc(OTf)_3$[21], microwave irradiation[22] and $Bi(NO)_3{\cdot}5H_2O$[23], montmorillonite KSF-clay[24]. Many of these methods have significant drawbacks *e.g.*, they involve expensive reagents, hazardous solvents, strongly acidic conditions, require longer reaction time, high temperatures, difficulties in work-up, use of stoichiometric quantities of reagents, incompatibility with other functional groups, product isolation, involve products that contribute to environmental pollution and low product yield. Therefore, the development of a less acidic alternative would extend the scope of the synthesis of 2,5-disubstituted pyrrole. Herewith, we report, trifluoroacetic acid (TFA) as a simple and efficient catalyst for the synthesis of 2,5-dimethyl-1-substituted pyrrole. The advantages of this catalyst are: it is readily available, economical, homogenous reaction conditions, simple product recovery process, easy to scale up and results in high yields. In this research we show that the substituted aryl/heteroaryl amine reacts efficiently with acetonylacetone in methylene dichloride (MDC) at room temperature in the presence of trifluoroacetic acid (**Scheme-I**).

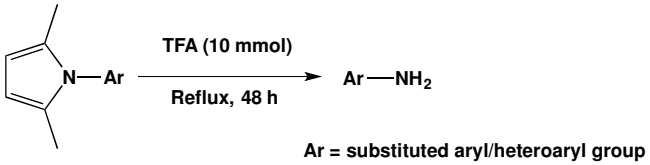


Ar = substituted aryl/heteroaryl group

Scheme-I: Synthesis of 2,5-dimethyl-1-substituted pyrrole by Paal-Knorr method

It was also observed that 2,5-dimethyl-1-substituted pyrroles can deprotect to substituted aryl/heteroaryl amines in excess of trifluoroacetic acid under reflux conditions in moderate yields. Hence, acetonylacetone can be used as amine protecting agent. Protection and deprotection of organic functionalities play an essential role in the elegant art of multistep organic synthesis. The presence of an amine function in many biologically active compounds makes its protection a

frequently needed exercise in medicinal chemistry. Generally amine can be protected by di-*tert*-butyl dicarbonate (Boc anhydride)[25], benzyl chloroformate (CBZ chloride)[26], allyl chloride[27,28], *N*-(9*H*-fluoren-2-ylmethoxycarbonyloxy) succinimide[27,29,30]. According to reported literature, these protecting groups are very sensitive to acidic, basic or catalytic hydrogenation conditions. Hence acetonylacetone could acts as an amine-protecting agent in multistep organic synthesis due to the stability of 2,5-dimethyl-1-substituted pyrroles (**Scheme-II**).



Scheme-II: Deprotection of 2,5-dimethyl-1-substituted pyrrole by trifluoroacetic acid to substituted aryl/heteroaryl amines

EXPERIMENTAL

Chemicals, solvents and catalysts were procured from Sigma Aldrich Company and used without further purification. TLC was performed on Merck 60 F_{254} silica gel plates. ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz Brucker spectrometer using $CDCl_3$ as a solvent. Chemical shifts (δ) were indicated in parts per million downfield from TMS. Mass spectra were recorded using LC-MS-Agilent 1100 series with MSD (ion trap) using 0.1 % aqueous trifluoo acetic acid in acetonitrile system on C_{18}-BDS column.

General procedure for the synthesis of 2,5-dimethyl-1-substituted pyrrole (1a-m): Aromatic/heteroaromatic amine (10 mmol), acetonylacetone (10 mmol) and trifluoroacetic acid (2 mmol) were taken in MDC (5 mL) under nitrogen atmosphere and stirred for about 1 h (monitored by thin layer chromatography). After completion of the reaction, it was quenched by 10 % sodium bicarbonate solution, extracted twice with MDC, dried and concentrated. The crude product was purified by column chromatography by eluting with *n*-hexane-ethyl acetate mixture (10-30 %). All the synthesized products were characterized by spectral data.

4-(2, 5-Dimethyl-1*H*-pyrrol-1-yl)-2-fluorophenol (1a): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.1 (s, 6H), 5.4 (s, 1H), 5.89 (s, 2H), 6.90-6.91 (m, 1H), 6.94-6.98 (d, 1H), 7.00-7.19 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 12, 109, 111, 117, 118, 132, 134, 141, 149. LC-MS: m/z = 212 (M^+).

2, 5-Dimethyl-1-[4-(trifluoromethyl)phenyl]-1*H*-pyrrole (1b)[31]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.1 (s, 6H), 5.9 (s, 2H), 7.36-7.38 (d, 2H), 7.7-7.8 (d, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 12, 111, 120, 121, 126, 128, 132, 144. LC-MS: m/z = 240 (M^+).

1-(4-Bromophenyl)-2, 5-dimethyl-1*H*-pyrrole (1c)[32,33]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (s, 6H), 5.91 (s, 2H), 7.09-7.18 (d, 2H), 7.57-7.60 (d, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 12, 111, 120, 123, 132, 133, 140. LC-MS: m/z = 251 (M^+).

2,5-Dimethyl-1-[(1R)-1-phenylethyl]-1*H*-pyrrole (1d)[21,34]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86-1.88 (d, 3H), 2.09 (s, 6H), 5.40-5.49 (m, 1H), 5.80 (s, 2H), 7.04-7.06 (t, 2H), 7.24-7.27 (m, 1H), 7.28-7.39 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13, 23, 44, 109, 125, 127, 128, 134, 140. LC-MS: m/z = 200 (M^+).

1-(4-Butyl-3-fluoro-phenyl)-2,5-dimethyl-1*H*-pyrrole (1e): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.0 (t, 3H), 1.33 (m, 2H), 1.62 (m, 2H), 2.0 (s, 6H), 2.5 (t, 2H), 5.7 (s, 2H), 6.9 (d, 2H), 7.1 (s, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 11, 14, 22, 24, 34, 107, 110, 115, 123, 130, 131, 139, 162. LC-MS: m/z = 245 (M^+).

[5-Chloro-2-(2, 5-dimethyl-1*H*-pyrrol-1-yl) phenyl](3-fluorophenyl)methanone (1f): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.9 (s, 6H), 5.5 (s, 2H), 6.96-7.08 (m, 1H), 7.08-7.10 (q, 1H), 7.20-7.25 (m, 1H), 7.30-7.31 (m, 2H), 7.58-7.67 (q, 1H), 7.68 (s, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13, 110, 117, 119, 121, 125, 129, 130, 131, 133, 139, 140, 161, 187. LC-MS: m/z = 328 (M^+).

Methyl [4-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenyl]acetate (1g): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04 (s, 6H), 3.5 (s, 3H), 3.7 (s, 2H), 5.91 (s, 2H), 7.16-7.18 (q, 2H), 7.27-7.38 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 12, 40, 52, 112, 121, 131, 132, 133, 140, 174. LC-MS: m/z = 244 (M^+).

N-[2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-4-methoxyphenyl]benzamide (1h): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.0 (s, 6H), 3.8 (s, 3H), 5.91 (s, 2H), 7.14-7.18 (q, 2H) 7.39-7.41 (t, 2H), 7.63-7.69 (m, 2H), 7.67 (s, 1H), 7.7 (s, 1H), 8.02-8.05 (q, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 12, 57, 108, 112, 113, 122, 123, 128, 129, 132, 133, 134, 135, 159, 166. LC-MS: m/z = 321 (M^+).

3-(2, 5-Dimethyl-1*H*-pyrrol-1-yl)quinoline (1i)[35]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.1 (s, 6H), 5.9 (s, 2H), 7.65-7.67 (d, 1H) 7.79-7.82 (q, 1H), 7.88-7.90 (d, 1H), 8.0 (d, 1H), 8.1-8.2 (d, 1H), 8.80-8.81 (d, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13, 108,126, 127, 128, 129, 130, 133, 141, 144. LC-MS: m/z = 222 (M^+).

4-(2, 5-Dimethyl-1*H*-pyrrol-1-yl)-2-methyl-1*H*-indole (1j): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 6H), 2.47 (s, 3H), 5.90 (s, 2H), 6.20-6.21 (q, 1H), 6.93-6.95 (q, 1H), 7.32-7.35 (m, 2H), 8.03-8.05 (s, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13, 100, 104, 110, 110.1, 119, 121, 129, 131, 135, 136. LC-MS: m/z = 225 (M^+).

7- (2,5-Dimethyl-1*H*-pyrrol-1-yl)-1H-indole (1k): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (s, 6H), 5.9 (s, 2H), 7.02-7.05 (q, 1H), 7.39-7.40 (d, 1H), 7.80-7.81 (q, 1H), 8.20-8.21 (d, 1H), 11.0 (br, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13, 105, 109, 112.1, 122, 122.4, 129, 134, 137, 140. LC-MS: m/z = 212 (M^+).

5-(2, 5-Dimethyl-1*H*-pyrrol-1-yl)-1-methyl-3-phenyl-1*H*-pyrazole (1m): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 6H), 3.5 (s, 3H), 5.9 (s, 2H), 6.59 (s, 1H), 7.2 (q, 1H), 7.41-7.45 (m, 2H), 7.82-7.86 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13, 25, 105, 108, 127, 128, 130, 132, 133, 149. LC-MS: m/z = 252 (M^+).

General procedure for the deprotection of 2,5-dimethyl-1-substituted pyrrole to substituted aryl/heteroaryl amine (2a-m): 2,5-Dimethyl-1-substituted pyrrole (1 mmol) was taken in 50 mL round bottom flask, trifluoroacetic acid (10 mmol) was added and refluxed for 48 h. Completion of reaction was monitored through thin layer chromatography. After reaction completion, the reaction was quenched by 10 % sodium bicarbonate solution and extracted twice with MDC,

dried and then concentrated. The crude product was purified by column chromatography by eluting with *n*-hexane-ethyl acetate mixture (0-50 %). All the products were characterized by spectral data.

TABLE-1
COMPARATIVE STUDY OF DIFFERENT CATALYST[a] USED IN THE PAAL-KNORR REACTION FOR PYRROLE SYNTHESIS

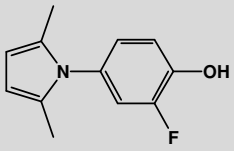
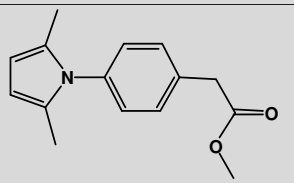
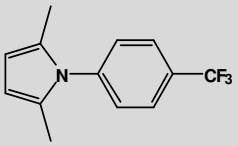
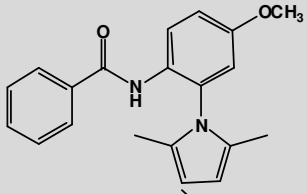
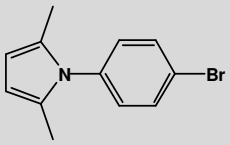
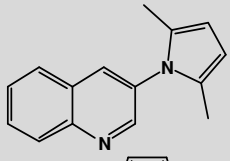
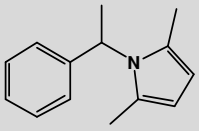
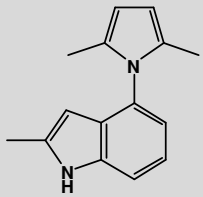
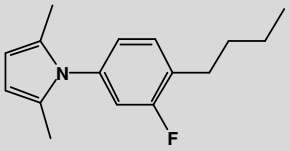
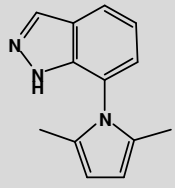
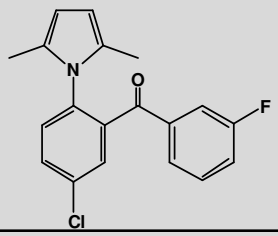
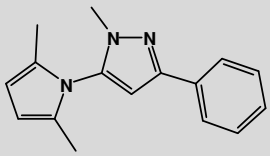
S. No.	Name of catalyst	Yield (%)
1	Trifluoroacetic acid	92
2	Iodine	40
3	Sulfamic acid	60
4	*p*-Toluene sulfonic acid	80
5	Sulfuric acid	40

[a]Present method reaction conditions: *p*-bromo aniline (10 mmol), acetonylacetone (10 mmol), catalyst (2 mmol) and MDC (5 mL) were stirred for 1 h at nitrogen atmosphere to yield **1c**.

RESULTS AND DISCUSSION

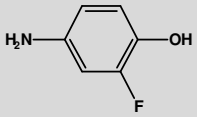
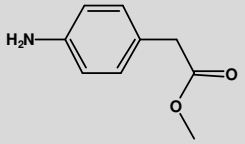
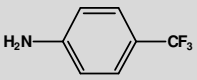
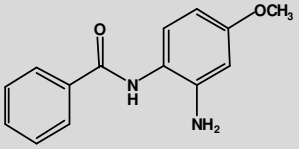
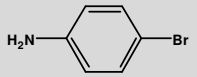
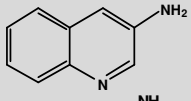
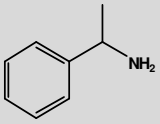
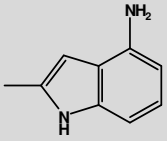
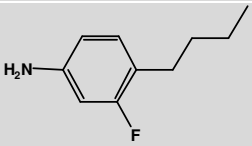
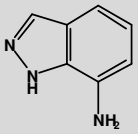
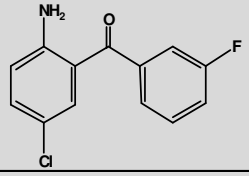
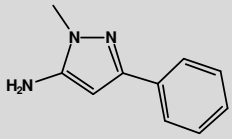
In this paper, we have reported an easy, efficient and selective method for Paal-Knorr pyrrole synthesis. Substituted aryl/heteroaryl amines smoothly reacted with acetonylacetone in the presence of trifluoroacetic acid at room temperature. MDC was found to be a good solvent for this reaction. To demonstrate the protocol, we selected substituted anilines as model substrates and treated them with acetonylacetone in the presence of trifluoroacetic acid (2 mmol) to get substituted pyrrole (**Scheme-I**) in excellent yields in Table-2 entry **1a**-**1m**. Interestingly substituted heterocyclic amines such as, quinolone, indole, indazole and pyrrazole amines yielded the corresponding pyrroles in excellent yields at 89, 98, 85 and 87 %, respectively (entry **1i**, **1j**, **1k** and **1m**). It was also observed that substituted benzophenone amine and substituted benzophenone amide undergo Paal-Knorr reaction smoothly to yield

TABLE-2
PAAL-KNORR REACTION OF ACETONYLACETONE WITH SUBSTITUTED ARYL/HETEROARYL AMINE IN THE PRESENCE OF TRIFLUOROACETIC ACID

Entry[a]	2, 5-Dimethyl-1-substituted pyrroles	Time (min)	Yield[b] (%) [ref]	Entry[a]	2, 5-Dimethyl-1-substituted pyrroles	Time (min)	Yield[b] (%) [ref]
1a		40	90	**1g**		50	90
1b		50	81[31]	**1h**		45	89
1c		47	92[32,33]	**1i**		45	89[35]
1d		45	89[21,34]	**1j**		30	98
1e		50	90	**1k**		50	85
1f		30	91	**1m**		45	87

[a]Novel compounds, **1a**, **1e, 1f**, **1g, 1h,1j, 1k,** and **1m** werecharacterized by NMR (^{1}H and ^{13}C) and LC-MS analysis. Compounds **1b**, **1c**, **1d** and **1i** were known compounds and were characterized by NMR (^{1}H and ^{13}C) and LC-MS analysis and compared with authentic sample.[b]Isolated yield.

TABLE-3
DEPROTECTION OF 2,5-DIMETHYL-1-SUBSTITUTED PYRROLE BY TRIFLUOROACETIC ACID UNDER REFLUX CONDITION

Entry	Substituted aryl/heteroaryl amine[a]	Time (h)	Yield[b] (%)	Entry	Substituted aryl/heteroaryl amine[a]	Time (h)	Yield[b] (%)
2a		48	49	**2g**		48	50
2b		48	56	**2h**		48	49
2c		48	49	**2i**		48	49
2d		48	50	**2j**		48	50
2e		48	49	**2k**		48	50
2f		48	60	**2m**		48	60

[a]All the compounds were characterized by NMR (^{1}H and ^{13}C) and LC-MS analysis and compared with authentic sample.[b]Isolated yield.

1f and **1h** at 91 and 89 %, respectively. As shown in Table-1 out of five catalyst used for the synthesis of substituted pyrrole in Paal-Knorr reaction, trifluoro- acetic acid emerged out as a promising catalyst by yielding 92 % of 1-(*p*-bromophenyl)-2, 5-dimethyl-1*H*-pyrrole **1c** when compared to other catalyst such as *p*-toluenesulfonic acid, sulfamic acid, iodine and sulfuric acid at 80, 60, 40 and 40 %, respectively.

Scheme-II also indicates that 2,5-dimethyl pyrroles can deprotect and yield the corresponding aryl/heteroaryl amines in the presence of trifluoroacetic acid at reflux condition. In multistep organic synthesis acetonylacetone can be used as an amine-protecting agent. Generally, we found that 10 mmol of trifluoroacetic acid is required for the completion of reaction over a period of 48 h. We have also found that some of the substituted pyrroles are highly stable and noticed that traces of the starting material remain after 2 days reflux condition. Yields of the products **1a**-**1m** were in the range of 49-60 % as shown in Table-3. Heterocyclic substituted pyrroles such as quinolone, indole, indazole and pyrrazole undergo deprotection smoothly and yielded **2i**, **2j**, **2k** and **2m**. We also found that substituted benzophenone and substituted amide functional groups survived under this experimental condition and yielded **2f** and **2h**.

Conclusion

We have established an efficient and simple method for Paal-Knorr pyrrole synthesis and its deprotection. Eight novel compounds **1a**, **1e, 1f**, **1g, 1h, 1j, 1k, 1m** and four known compounds **1b**, **1c**, **1d** and **1i** were prepared and structurally characterized using spectroscopic technique. The yield of the products **1a**-**1m** was found to be excellent at 81-98 %. The deprotection of title compounds **1a**-**1m** using trifluoroacetic acid to yield the respective substituted anilines **2a-2m** in the satisfactory yield at 49-60 %.

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