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1, 4-Diazabicyclo[2.2.2]octanium diacetate: An effective, mild and reusable catalyst for the synthesis of 2,4,5–trisubstituted imidazoles

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ABSTRACT

1, 4-Diazabicyclo[2.2.2]octanium diacetate supplies an environmentally friendly procedure for the synthesis of 2,4,5-trisubstituted imidazoles through one-pot multicomponent condensation of benzyl or benzoin and ammonium acetate with various aldehydes. These compounds were obtained in high yields and short reaction times. The catalyst could be easily recovered and reused for five cycles with almost consistent activity. All of synthesized compounds were characterized by their physical constant, comparison with authentic samples, IR, ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis.

1. Introduction

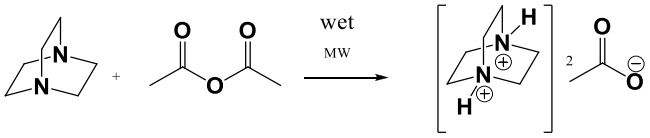
The imidazole substructures were found in a large number of pharmacologically active compounds and natural products such as the hypnotic agent etomidate, amino acid histidine [1], the proton pump inhibitor omeprazole [2], the antiulcerative agent cimetidine [3], B-Raf kinase [4], cyclooxygenase-2 (COX-2) [5], biosynthesis of interleukin-1 (IL-1) [6], plants growth regulators [7], anti-bacterial [8], pesticide [9], herapeutic agents [10], antitumour [11], modulators of P-glycoprotein (P-gp)-mediated multidrug resistance (MDR) [12], and also CB1 cannabinoid receptor antagonists [13].

In 1882, Radziszewski and Japp [14, 15] reported the first synthesis of a highly substituted imidazole from a 1,2-dicarbonyl compound, aldehydes and ammonia. In recent years, the synthesis of 2,4,5-trisubstituted imidazoles have been performed by various catalysts [16-27].

Most of these described procedures have some serious defects, such as tedious work-up and purification, significant amounts of toxic waste materials, highly acidic conditions, long reaction time, occurrence of side reactions, low yields, the use of expensive reagents or catalysts, low selectivity and high temperatures in refluxing or microwave condition. Therefore, in continuation of reported works to use green condition for the synthesis of organic compounds [26, 27] , the development of easy, green, effective, high-yielding, and eco-friendly approaches using novel catalysts for the synthesis of imidazoles is an important research topic for organic chemists.

2. Results and Discussion

As a part of our going interest for the development of efficient and environmentally friendly procedures for the synthesis of heterocyclic and pharmaceutical compounds [28-35], a new, efficient, facile and fast procedure was introduced for the synthesis of 2,4,5-triaryl-1H-imidazoles using the reaction between aldehydes 1, 1,2-Diketone 2 or α-hydroxyketone 3 and ammonium acetate in the presence of synthesized dicathionic acidic ionic liquid 1,4-diazabicyclo[2.2.2]octanium diacetae (Scheme 1).



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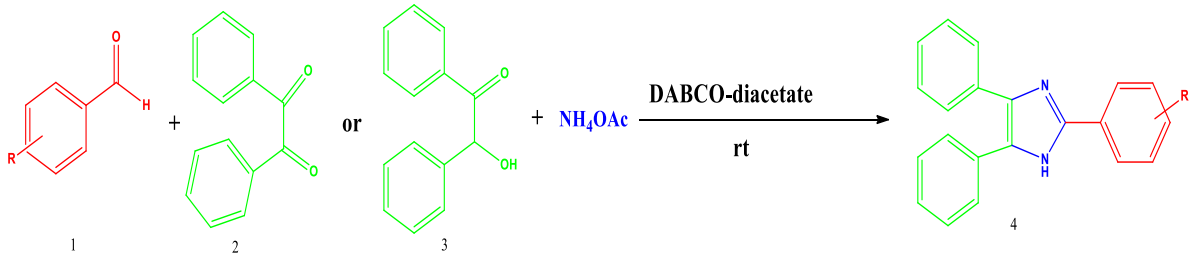


Scheme 1. Synthesis of DABCO-diacetate and 2,4,5-triarylimidazoles

First for selecting the effective catalyst amount, the reaction of benzoin **3**, benzaldehyde **1a**, and ammonium acetate was tested in different amounts of DABCO-diacetate. The results are shown in Figure 1. As can be seen, the best result was obtained with 0.5mmol IL and increasing the amount of IL had no obvious effect on yield. Notably, the desired product could not be obtained under similar reaction conditions, even after a long time (360 min) in the absence of the catalyst.

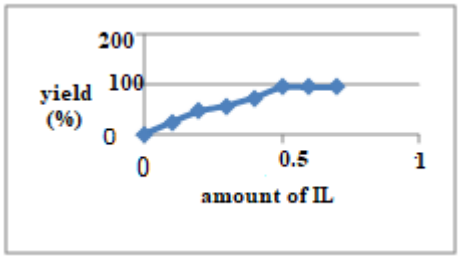
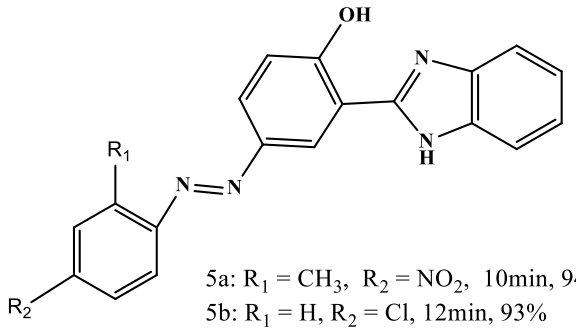


Figure 1. Effect of the amounts of DABCO-diacetate for the synthesis of **4a**

To present the efficiency and generality of the reaction, various aldehydes were reacted with benzoin and ammonium acetate in the presence of DABCO-diacetate. The results are summarized in Table 1. It is seen that various aromatic aldehydes having both electron-releasing and electron-withdrawing substituents in the ortho, meta and para positions, aliphatic and heterocyclic aldehydes afford high yields of the products. Another important aspect of this method is the survival of a variety of functional groups such as methoxy under these acidic conditions.

Benzil 2 are usually synthesized from α-hydroxy ketones like benzoin 3 catalyzed by various oxidants. Some of these oxidants are expensive, toxic, and require tedious work-up [36]. To avoid the preparation of the 1,2-diketone, and to improve the reaction yield and time, the synthesis of 2,4,5-triphenyl-1H-imidazole was studied using benzyl (Table 1).

In continuation of our study, we triggered to synthesize a category of azodispersive imidazole dyes using the reaction of azo-linked aldehyde with 1,2-diaminobenzene in the presence of DABCO-diAc. The results are shown in Figure 2.



5a: $R_1 = CH_3$, $R_2 = NO_2$, 10min, 94%
5b: $R_1 = H$, $R_2 = Cl$, 12min, 93%
5c: $R_1 = Cl$, $R_2 = H$, 8min, 98%
5d: R_1 , $R_2 = Cl$ 13min, 94%

Figure 2. Synthesis of azodispersive imidazole dyes catalyzed by DABCO-diacetate

To check the efficiency of this method, the comparison between this method and some of previous reported methods (various ionic liquids) for the synthesis of 4a was carried out (Table 2).

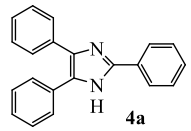
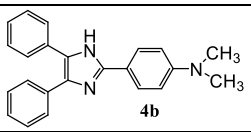
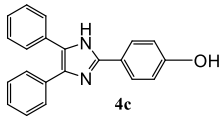
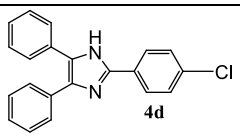
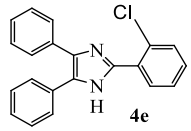
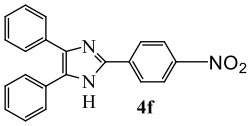
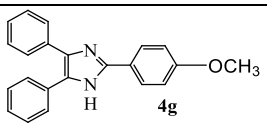
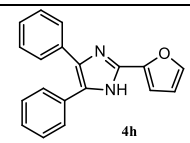
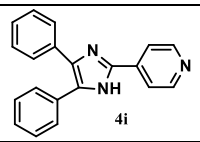
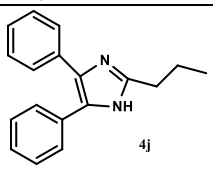
Table 2. Comparison of synthesis of compound **4a** in this method with some of previous reported methods

Catalyst	Condition	time / min	Yield, %	Ref.
[Hmim]TFA	Heat, 80 °C	30	97	[37]
$[Bnmim]HSO_4$	MW	5	95	[38]
[DodecIm] HSO_4	EtOH, rt	300	98	[39]
$[Bmim]PF_6$	H_2O, reflux	120	92	[40]
[Hmim]THF	H_2O, rt	10	88	[41]
DABCO-diacetate	rt[b]	10	96	This work
	rt[c]	6	98	

a. The used aryl aldehyde is 4-Chlorobenzaldehyde. b. the used substrate is benzoin. c. the used substrate is benzyl.

After reaction, the dissolved ionic liquid in water is distilled under vacuum for recovery and reuse. After five successive runs, recycled ionic liquid showed no loss of efficiency with regard to reaction time and yield (Table 3).

Table 1. Synthesis of imidazole derivatives catalyzed by DABCO-diacetate[a]

Entry	product	Benzil (2)		Benzoin (3)		M.P (°C)	
		Time (min)	Yield (%)a, b	Time (min)	Yield (%)a, b	Found	Reported [39]
1	 **4a**	6	98	10	96	269-271	272-274
2	 **4b**	9	96	12	94	235-237	238-240
3	 **4c**	10	93	12	93	228-229	226-228
4	 **4d**	6	98	10	97	266-267	262-264
5	 **4e**	11	95	13	94	186-188	190-191
6	 **4f**	6	97	11	94	223-225	223-225
7	 **4g**	10	94	13	95	227-228	228-231
8	 **4h**	8	95	15	94	220-221	221-223
9	 **4i**	10	94	12	95	278-280	276-278
10	 **4j**	8	96	11	94	243-244	243-244

a. Isolated yields

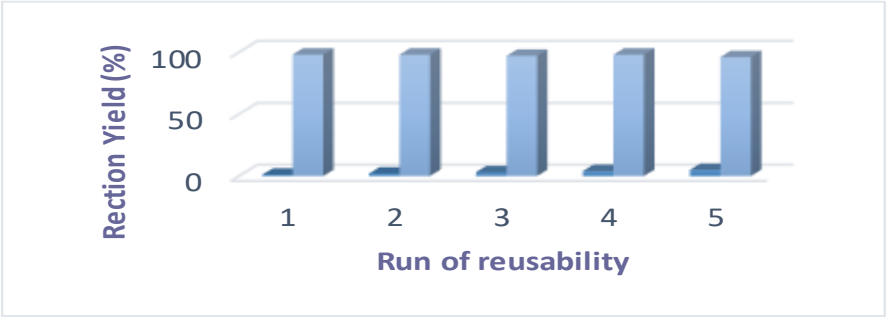


Figure 3. Reusability of DABCO-diacetate for the synthesis of 4a

3. Experimental

Chemicals were purchased from Merck and Fluka. All solvents used were dried and distilled according to standard procedures. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were determined on a Shimadzu FT-IR 8600 spectrophotometer. ^{1}H and ^{13}C NMR spectra were determined on a Bruker 400 DRX Avance instrument at 400 and 100 MHz. Elemental analyses were recorded on a Carlo-Erba EA1110CNNO-S analyzer.

General Procedure for the synthesis of [DABCO]dihydroacetate(1,4diazabicyclo[2.2.2]octani um diacetate) The ionic liquid DABCO-diacetate was synthesized by Zare Fekri, et al. [27-30, 35]. But, in the new experiment, we synthesized this ionic liquid under ultrasound irradiation with higher yield and cleaner condition instead of microwave irradiation reported in literature. Analytical data for DABCO-dihydroacetate: yellow oil. ^{1}H NMR (400MHz, $CDCl_3$): δ = 2.16 (s, 6H), 3.01 (s, 12H), 14.11 (s, 2H) ppm. ^{13}C NMR (100MHz, $CDCl_3$): δ = 22.0, 44.5, 175.9 ppm.

General procedure for the DABCO-diacetate-catalyzed synthesis of 4a-j

A mixture of aldehyde (1 mmol), benzil or benzoin (1 mmol), ammonium acetate (1 mmol) and [DABCO] diacetate (0.5 mmol) were stirred at room temperature for the required reaction time according to Table 1. After completion of reaction, as indicated by TLC, the reaction mixture was resolved in 20 mL of H_2O. The product was separated by filtration and recrystallized from EtOH and dried to afford powdery compounds of 4a-j or 5a-d. The filtrate was concentrated under reduced pressure and washed with diethyl ether. Then, it dried in a vacuum evaporator to recover the ionic liquid for subsequent use. All of synthesized compounds are known and were characterized by their physical constant, comparison with authentic samples, IR, ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis.

General procedure for the DABCO-diacetate-catalyzed synthesis of 5a-d

A mixture of azo linked aldehyde (1 mmol) and 1,2-diaminobenzene (1 mmol) and [DABCO] diacetate (0.5 mmol) were stirred at room temperature for the required reaction time according to Figure 2. After completion of reaction, as indicated by TLC, the reaction mixture was resolved in 20 mL of H_2O. The product was separated by filtration and recrystallized from EtOH and dried to afford powdery compounds of 5a-d. All of synthesized compounds are unknown and new and were characterized by their mp, IR, ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis.

Data for new synthesized compounds

(E)-2-(1H-benzo[d]imidazol-2-yl)-4-((2-methyl-4-nitrophenyl)diazenyl) phenol (5a)

This compound was obtained as Dark brown solid, mp 195-198 °C, IR (KBr): 3361, 3280 (aromatic N-H or O-H stretching), 3035 (aromatic C-H stretching), 2959 (aliphatic C-H stretching), 1626 (N=N stretching), 1583, 1456 (aromatic C=C stretching), 1341 (C-N stretching), 1284 (C-O stretching) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): 2.10 (s, 3H, CH_3), 6.67 (d, J = 8.8 Hz, 1H), 6.99 (s, 1H), 7.06 (s, 1H), 7.38-7.76 (m, 3H), 7.84-7.90 (m, 2H), 8.14-8.27 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): 17.69, 122.61, 123.59, 124.52, 125.86, 126.19, 126.32, 126.56, 126.66, 127.66, 128.22, 131.10, 131.75, 136.15, 139.16, 145.91, 154.40 ppm. Anal.calcd. for $C_{20}H_{15}N_5O_3$: C, 64.34; H, 4.05; N, 18.76. Found: C, 64.37; H, 4.09; N, 18.78.

(E)-2-(1H-benzo[d]imidazol-2-yl)-4-((4-chlorophenyl)diazenyl)phenol (5b)

This compound was obtained as Dark brown solid, mp 269-272 °C, IR (KBr): 3402 (N-H stretching), 3204 (OH stretching), 3057 (aromatic C-H stretching), 1623 (N=N stretching), 1560 (aromatic C=C stretching), 1483 (aromatic C=C stretching), 1317 (C-N stretching), 1249 (C-O stretching), 1087 (C-Cl stretching) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): 7.24 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.8 Hz, 1H), 7.40- 7.49 (m, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.78-7.85 (m, 2H), 7.91 (d, J = 8.4 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): 126.54, 127.28, 127.89, 129.21, 129.60, 129.89, 130.15, 132.77, 134.30, 134.74, 134.89, 136.07, 145.40, 150.89 ppm. Anal. calcd. for $C_{19}H_{13}ClN_4O$: C, 65.43; H, 3.76; N, 16.06. Found: C, 65.41; H, 3.77; N, 16.01.

(E)-2-(1H-benzo[d]imidazol-2-yl)-4-((2-chlorophenyl)diazenyl)phenol (5c)

This compound was obtained as Dark brown solid, mp 245-250 °C, IR (KBr): 3330 (aromatic N-H or O-H stretching), 3061 (aromatic C-H stretching), 1623 (N=N stretching), 1598, 1498 (aromatic C=C stretching), 1462 (C=N stretching), 1389 (C-N stretching), 1266 (C-O stretching), 1126 (C-Cl stretching) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): 7.04-7.09 (m, 1H), 7.21- 7.29 (m, 1H), 7.33- 7.40 (m, 3H), 7.42- 7.50 (m, 1H), 7.52- 7.591 (m, 1H), 7.596- 7.65 (m, 1H), 7.66- 7.75 (m, 1H), 7.76- 7.90 (m, 1H), 7.92-7.95 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): 119.07, 123.79, 124.34, 124.70, 125.70, 127.19, 127.24, 127.32, 127.64, 128.06, 129.44, 130.48, 130.64, 131.11, 134.63, 145.47 ppm. Anal. calcd. for

$C_{19}H_{13}ClN_4O$: C, 65.43; H, 3.76; N, 16.06. Found: C, 65.45; H, 3.79; N, 16.06.

(E)-2-(1H-benzo[d]imidazol-2-yl)-4-(phenyldiazenyl)phenol (5d)

This compound was obtained as Dark brown solid, mp 270-273 °C, IR (KBr): 3348 (aromatic N-H or O-H stretching), 3057 (aromatic C-H stretching), 1620 (N=N stretching), 1594 (aromatic C=C stretching), 1595 (aromatic C=C or C=N stretching), 1391 (C-N stretching), 1264 (C-O stretching) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): 7.29 (d, J = 8.8 Hz, 1H), 7.37 (dd, J = 3.2 Hz, J = 6.4 Hz, 2H), 7.55- 7.62 (m, 2H), 7.64-7.68 (m, 2H), 7.75(dd, J = 3.2 Hz, J = 6.0 Hz, 2H), 7.92 (d, J = 7.8 Hz, 1H), 8.02 (dd, J = 2.4 Hz, J = 8.8 Hz, 2H), 13.00-14.50 (brs, 2H) ppm. ^{13}C NMR (CDCl3, 62.5 MHz): 123.43, 124.03, 126.15, 128.71, 129.63, 129.72, 130.01, 130.57, 131.54, 132.07, 139.50, 143.86, 145.47, 150.78 ppm. Anal. calcd. for $C_{19}H_{14}N_4O$: C, 72.60; H, 4.49; N, 17.82. Found: C, 72.64; H, 4.51; N, 17.83.

4. Conclusion

In conclusion, we have investigated DABCO-diacetate as a mild and efficient catalyst for the synthesis of 2,4,5-triarylimidazoles. The remarkable advantages offered by this method are: catalyst is inexpensive, non-toxic, easy handling and reusable. On the other hand, simple work-up procedure, short reaction time, high yields of product with better purity and green aspect by avoiding toxic catalyst and hazardous solvent are another advantages of this method. To the best of knowledge, this is the first synthesis of trisubstituted imidazoles in the presence of dicationic ionic liquid DABCO-diacetate.

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