Novel Four-Component Approach for the Synthesis of Polyfunctionalized 1,4-Dihydropyridines in Aqueous Media

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Dedicated to Prof. *Hooshang Pirelahi* on the occasion of his 70th birthday

The four-component reaction of dimethyl acetylenedicarboxylate (=dimethyl but-2-ynedioate; DMAD), aromatic aldehydes, and malononitrile (=propanedinitrile) leads to polyfunctionalized 1,4-dihydropyridine derivatives. The reaction proceeds at room temperature and in the presence of a catalytic amount (20%) of $(NH_4)_2HPO_4$ as a base in aqueous media.

Introduction. – Construction of complex molecules by using a one-pot multi-component reaction (MCR) is a significant pathway in organic synthesis. This type of reaction becomes increasingly important in organic, bioorganic, and medicinal chemistry for the synthesis of polyfunctionalized molecules. MCRs have been applied to generate highly diverse combinatorial libraries with high bond-forming efficiency (BFE). Thus, there is a strong demand for the development of new MCRs that allow to prepare an assembly of polyfunctionalized heterocycles [1].

The core structure of *N*-substituted dihydropyridines (DHPs) is an important heterocyclic framework that can be found in numerous biologically active compounds. For example, some of these compounds are Ca^{2+}-channel blocker and show antihypertensive effects [2]. A series of cage-dimeric *N*-substituted 1,4-dihydropyridines was evaluated as inhibitors of membrane efflux pump in multidrug-resistant cancer [2][3][4]. Thus, the synthesis of 1,4-dihydropyridines is an important and useful task in organic chemistry. So far, many protocols for the synthesis of DHPs have been reported [5]. A well-known approach is the *Hantzsch* reaction [4][6]. Cyclocondensation of aldehydes, propiolates (=prop-2-ynoates), and $AcO(NH_4)$ or primary amines in refluxing AcOH or under microwave irradiation leads to 4-substituted *N*-alkyl-1,4-dihydropyridines [7].

As a part of our current studies on the development of new routes in heterocyclic synthesis *via* novel one-pot MCRs [8], we report here a novel four-component reaction for the synthesis of polyfunctionalized 1,4-dihydropyridines in aqueous media at room temperature in good yields (*Scheme 1*). The reaction was performed in the presence of catalytic amounts of $(NH_4)_2HPO_4$ (20%). The obtained products contain one C≡N,

Scheme 1

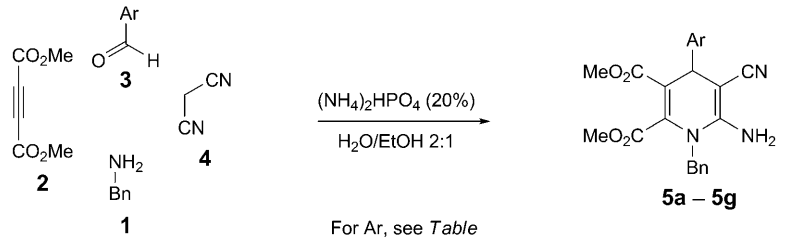


Table. *Synthesis of Polyfunctionalized 1,4-Dihydropyridines* via *a Four-Component One-Pot Reaction at Room Temperature* (see *Scheme 1*)

Ar	Product	Time [h]	Yield [%][a])
Ph	**5a**	20	79
4-Br–C_6H_4	**5b**	16	75
4-Cl–C_6H_4	**5c**	14	85
4-N≡C–C_6H_4	**5d**	12	95
3-OH–C_6H_4	**5e**	24	80
3-NO_2–C_6H_4	**5f**	10	98
4-NO_2–C_6H_4	**5g**	10	87

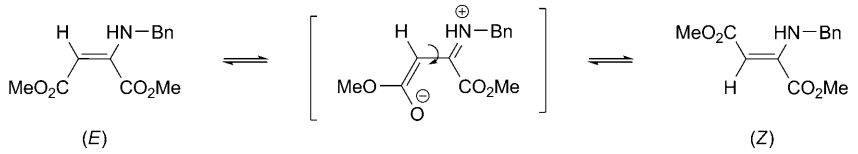
[a]) Yield of isolated product.

one NH_2 group, and two ester groups, which could be readily used for further conversions. The results are summarized in the *Table*.

Results and Discussion. – The addition of nucleophiles across C≡C bonds has evolved to become a versatile tool for the synthesis of compounds with different functional groups [9]. Typically, the addition of amines to acetylenedicarboxylate (= but-2-ynedioate) derivatives has been extensively studied [10], and the DMAD–primary-amine adducts are used as efficient starting materials for the synthesis of heterocyclic skeletons (DMAD = dimethyl but-2-ynedioate) [11].

In our experiments, the addition of benzylamine (**1**) to DMAD (**2**) under neat conditions was studied, which led to a mixture of (*Z*)/(*E*) isomers. In solution, the (*E*) isomer converts slowly to the (*Z*) isomer (see [12]) (*Scheme 2*). Reaction of benzylamine with DMAD was completed in less than 3 h under neat conditions. The assignments of the (*E*) and (*Z*) configurations of the DMAD–benzylamine adduct are based on the chemical shifts of the olefinic and NH H-atoms in the ^{1}H-NMR spectra.

Scheme 2



The olefinic H-atom of the (*E*) and (*Z*) isomer appeared at δ(H) 4.70 and 5.10, respectively [12], and the NH H-atom of the (*E*) and (*Z*) isomer resonated at δ(H) 5.20 and 8.40, respectively. The olefinic H-atom of the (*Z*) isomer appears at lower field as a result of anisotropic deshielding by the ester C=O groups. There is an efficient intramolecular H-bonding in the structure of (*Z*) isomer. It was shown that the ease of isomerization is related to the polarity of the solvent [13].

After formation of the DMAD–benzylamine adduct, a mixture containing the aromatic aldehyde **3**, malononitrile (= propanedinitrile; **4**), and 20% $(NH_4)_2HPO_4$ (DAHP) in H_2O/EtOH 2 : 1 was added to the adduct. The results for different aromatic aldehydes are summarized in the *Table*. The four-component reaction of benzylamine, DMAD, 4-chlorobenzaldehyde, and malononitrile was selected as a model, and the effect of different solvents and bases were studied. The yields of this model reaction (product **5c**) in MeCN, CH_2Cl_2, MeOH, and H_2O were 30, 25, 60, and 85%, respectively. Carrying out the model reaction in the presence of 10% 1-methyl-1*H*-imidazole or 10% DAHP as the base led to lower yields (24 and 14%, resp.). Meanwhile, different primary amines were used instead of benzylamine under the optimum conditions, for example, butylamine and aniline, but the best yield was obtained with benzylamine. The amount of DAHP as a base was also optimized, and the best yield for the synthesis of **5a**–**5g** was obtained with 20% DAHP.

The structure of compounds **5a**–**5g** were deduced from their spectroscopic and mass spectrometric data, which displayed in each case the molecular-ion peak at the appropriate *m*/*z* values. The ^{1}H-NMR spectra of **5d** in $CDCl_3$ showed two *s* at δ(H) 3.30 and 3.79 for two MeO groups. A distinguished signal for all of these compounds appeared at δ(H) 4.15–4.75 as a *s* which is due to H–C(4). The ^{13}C-NMR spectra of **5a**–**5g** exhibited a characteristic signal at δ(H) 37.9–38.6 for C(4). Furthermore, an unusual signal at δ(H) 60–66 for C(5) bearing the C≡N group could be explained by to the resonance structures displayed in the *Figure*. The ^{1}H- and ^{13}C-NMR spectra of **5a**–**5g** were similar to those of **5d**, except for the signals of the aryl moieties, which showed characteristic resonances in the appropriate regions of the spectra [10].

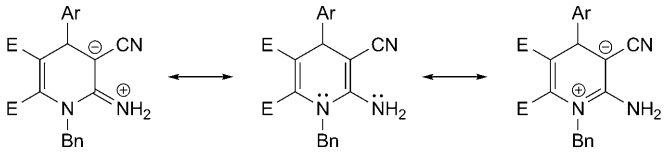
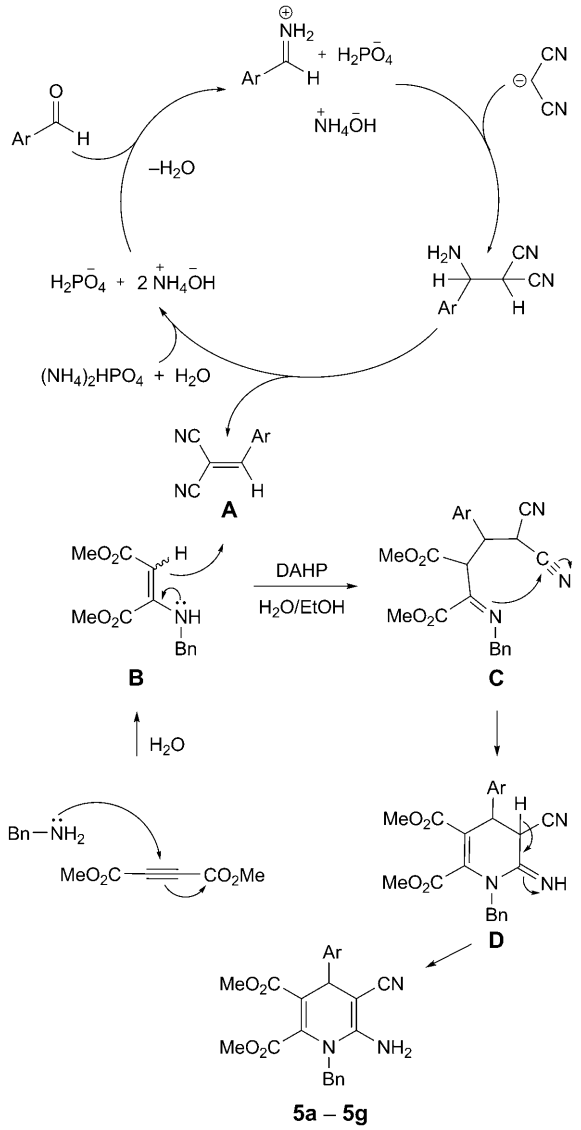


Figure. *Resonance structures of the CN-substituted 1,4-Dihydropyridines* **5a**–**5g**

To explain the mechanism of this multicomponent reaction, we propose a plausible reaction pathway which is shown in *Scheme 3*. *Knoevenagel* condensation of an aldehyde with malononitrile in the presence of DAHP as mild-base catalyst leads to the formation of 2-arylidenemalononitrile **A**. Reaction of benzylamine with dimethyl acetylenedicarboxylate gives the enamine **B**. Then, *Michael* addition of **B** to **A** yields adduct **C**, which is transformed to intermediate **D** *via* intramolecular addition of the N-atom as a nucleophile to the C≡N bond. The tautomerization of the imino group to the

Scheme 3. *Possible Mechanism for the Synthesis of Polyfunctionalized 1,4-Dihydropyridines* **5a**–**5g**



NH_2 group then forms the desired products **5a**–**5g**. Thus, the reaction could proceed *via* a domino *Knoevenagel*/*Michael* addition/cyclization reaction sequence.

For the investigation of the reaction mechanism, the 2-arylidenemalononitriles **A** were formed from the reaction of benzaldehydes and malononitrile, and then these were added to the benzylamine–DMAD adduct. The products were again **5a**–**5g**, but obtained in lower yields (30–73%) compared to our one-pot method, and also longer reaction times were required (12–36 h).

Conclusions. – We demonstrated a convenient synthesis of polyfunctionalized 1,4-dihydropyridine derivatives *via* a one-pot four-component reaction of benzylamine, DMAD, aromatic aldehydes, and malononitrile in the presence of a catalytic amount (20%) of DAHP at room temperature in aqueous media. The advantage of the present procedure is that the reaction is performed under neutral conditions by simple mixing of the starting materials, in good to high yields, with short reaction times, with 100% atom-economy, with high bond-forming efficiency (BFE), and finally in aqueous media under one-pot conditions.

S. B. would like to thank the *Iran National Science Foundation* (INSF) for the financial support. We thank Prof. *Rolf Gleiter* for his invaluable comments. Partial support of this work by the *Research Council of* K. N. Toosi *University of Technology* is appreciatively acknowledged.

Experimental Part

General. Commercially available materials were used without further purification. M.p.: *Electrothermal-9100* apparatus; uncorrected. IR Spectra: *ABB-FT-IR* (*FTLA 2000*) spectrometer; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-DRX-300-Avance* spectrometer; at 300 (^1H) and 75 MHz (^{13}C); $CDCl_3$ as solvent; δ in ppm rel. to Me_4Si as internal standard, J in Hz. GC/MS: *Hewlett-Packard-5973* (EI, 70 eV) instrument; in m/z (rel. %). Elemental analyses: *Heraeus-CHN-O* rapid analyzer for C, H, and N.

Polyfunctionalized 1,4-Dihydropyridines: General Procedure. A mixture of DMAD (2 mmol, 0.288 g) and benzylamine (2.4 mmol, 0.26 ml) was stirred vigorously at r.t. for 3 h (magnetic stirrer). Then, a mixture of benzaldehyde derivative (2 mmol), malononitrile (2 mmol, 0.133 g), and $(NH_4)_2HPO_4$ (20%, 26.4 mg) in H_2O/EtOH 2:1 (10 ml) was added and stirred at r.t. for 10–24 h (TLC monitoring). The solvent was evaporated and the precipitate purified by recrystallization from petroleum ether/CH_2Cl_2.

Dimethyl 6-Amino-1-benzyl-5-cyano-1,4-dihydro-4-phenylpyridine-2,3-dicarboxylate (**5a**): Yield 318 mg (79%). M.p. 89–93° (dec.). IR ($CHCl_3$): 3491, 3372, 3019, 2187, 1739, 1707, 1650, 1573. ^1H-NMR: 3.63 (*s*, MeO); 3.75 (*s*, MeO); 4.08 (br. *s*, NH_2); 4.60 (*s*, H–C(4)); 4.69 (*B* of *AB*, $J = 18$, 1 H, PhCH_2); 4.79 (*A* of *AB*, $J = 18$, 1 H, PhCH_2); 7.19–7.42 (*m*, 10 arom. H). ^{13}C-NMR: 38.4; 50.8; 52.2; 53.1; 66.7; 107.1; 120.3; 126.5; 126.9; 127.1; 128.5; 128.7; 129.3; 135.2; 142.1; 144.0; 151.0; 164.7; 165.8. EI-MS (70 eV): 403 (M^+), 326 (14), 344 (48), 91 (100), 106 (49). Anal. calc. for $C_{23}H_{21}N_3O_4$ (403.44): C 68.47, H 5.24, N 10.41; found: C 68.29, H 5.15, N 10.30.

Dimethyl 6-Amino-1-benzyl-4-(4-bromophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate (**5b**). Yield 361 mg (75%). M.p. 146–148° (dec.). IR ($CHCl_3$): 3432, 3345, 2945, 2188, 1744, 1697, 1576. ^1H-NMR: 3.64 (*s*, MeO); 3.77 (*s*, MeO); 4.15 (br. *s*, NH_2); 4.56 (*s*, H–C(4)); 4.67 (*B* of *AB*, $J = 17.5$, 1 H, PhCH_2); 4.79 (*A* of *AB*, $J = 17.5$, 1 H, PhCH_2); 7.05 (*d*, $J = 8.4$, 2 arom. H); 7.28 (*d*, $J = 8.4$, 2 arom. H); 7.30–7.43 (*m*, 5 arom. H). ^{13}C-NMR: 38.0; 50.8; 53.5; 54.1; 66.2; 106.7;120.0; 121.1; 126.6; 128.7; 129.2; 131.7; 134.9; 142.2; 143.0; 151.1; 164.5; 165.5. EI-MS (70 eV): 483 (31, $[M+2]^+$), 481 (20, M^+), 326 (72), 91 (100). Anal. calc. for $C_{23}H_{20}BrN_3O_4$ (482.33): C 57.27, H 4.18, N 8.71; found: C 57.13, H 4.10, N 8.71.

Dimethyl 6-Amino-1-benzyl-4-(4-chlorophenyl)-5-cyano-1,4-dihydropyridine-2,3-dicarboxylate (**5c**). Yield 371 mg (85%). M.p. 146–148° (dec.). IR (KBr): 3357, 3530, 2959, 2186, 1726, 1646, 1578. ^1H-NMR: 3.64 (*s*, MeO); 3.77 (*s*, MeO); 4.18 (br. *s*, NH_2); 4.57 (*s*, H–C(4)); 4.66 (*B* of *AB*, $J = 18$, 1 H, PhCH_2); 4.80 (*A* of *AB*, $J = 18$, 1 H, PhCH_2); 7.10 (*d*, $J = 8.4$, 2 arom. H); 7.18–7.29 (*m*, 5 arom. H); 7.28 (*d*, $J = 8.4$, 2 arom. H). ^{13}C-NMR: 37.9; 50.8; 52.1; 53.1; 66.2; 106.9; 120.1; 126.7; 126.9; 128.4; 128.7; 128.8; 129.3; 132.9; 135.0; 142.2; 142.5; 151.1; 164.5; 165.5. EI-MS (70 eV): 439 (10, $[M+2]^+$), 437 (28, M^+), 378 (66), 346 (14), 326 (30), 91 (100), 43 (42). Anal. calc. for $C_{23}H_{20}ClN_3O_4$ (437.88): C 63.09, H 4.60, N 9.60; found: C 62.90, H 4.50, N 9.47.

Dimethyl 6-Amino-1-benzyl-5-cyano-4-(4-cyanophenyl)-1,4-dihydropyridine-2,3-dicarboxylate (**5d**). Yield 406 mg (95%). M.p. 129–131° (dec.). IR (KBr): 3490, 3349, 2227, 2187, 1726, 1652, 1579. ^1H-NMR: 3.63 (*s*, MeO); 3.71 (*s*, MeO); 4.27 (br. *s*, NH_2); 4.63 (*s*, H–C(4)); 4.65 (*B* of *AB*, $J = 18$, 1 H, PhCH_2); 4.80

(*A* of *AB*, *J* = 18, 1 H, PhCH_2); 7.25 (*d*, *J* = 9.0, 2 arom. H); 7.28–7.39 (*m*, 5 arom. H); 7.54 (*d*, *J* = 9.0, 2 arom. H). ^{13}C-NMR: 38.6; 50.9; 52.3; 53.3; 53.4; 65.3; 106.2; 110.9; 118.7; 119.8; 126.7; 127.7; 128.8; 129.3; 132.6; 134.7; 142.6; 148.9; 151.4; 164.3; 165.2. EI-MS (70 eV): 428 (32, M^+), 369 (61), 326 (47), 337 (25), 106 (43), 91 (100). Anal. calc. for $C_{24}H_{20}N_4O_4$ (428.45): C 67.28, H 4.70, N 13.07; found: C 67.09, H 4.60, N 12.95.

Dimethyl 6-Amino-1-benzyl-5-cyano-1,4-dihydro-4-(3-hydroxyphenyl)pyridine-2,3-dicarboxylate (**5e**). Yield 327 mg (78%). M.p. 144–146° (dec.). IR (KBr): 3430, 3353, 2179, 1726, 1688, 1651, 1586. ^{1}H-NMR: 3.68 (*s*, MeO); 3.83 (*s*, MeO); 4.10 (br. *s*, NH_2); 4.54 (*s*, H–C(4)); 4.65 (*B* of *AB*, *J* = 17.5, 1 H, PhCH_2); 4.80 (*A* of *AB*, *J* = 17.5, 1 H, PhCH_2); 6.51 (*s*, 1 arom. H); 6.70 (*dd*, *J* = 8.0, 1 arom. H); 6.80 (*d*, *J* = 8.1, 1 arom. H); 7.16 (*t*, *J* = 8.1, 1 arom. H); 7.30–7.40 (*m*, 5 arom. H). ^{13}C-NMR: 38.0; 49.4; 51.9; 53.0; 60.8; 105.7; 113.6; 117.0; 121.3; 127.6; 128.2; 128.8; 129.2; 136.0; 142.6; 145.9; 151.6; 157.2; 164.1; 165.2. EI-MS (70 eV): 419 (57, M^+), 326 (60), 360 (80), 91 (100), 106 (12). Anal. calc. for $C_{23}H_{21}N_3O_5$ (419.44): C 65.86, H 5.04, N 10.01; found: C 65.62, H 4.95, N 9.90.

Dimethyl 6-Amino-1-benzyl-5-cyano-1,4-dihydro-4-(3-nitrophenyl)pyridine-2,3-dicarboxylate (**5f**). Yield 439 mg (98%). M.p. 175–177° (dec.). IR (KBr): 3414, 3360, 2941, 2180, 1740, 1709, 1652, 1531, 1421, 1343. ^{1}H-NMR: 3.66 (*s*, MeO); 3.77 (*s*, MeO); 4.21 (br. *s*, NH_2); 4.72 (*s*, H–C(4)); 4.74 (*B* of *AB*, *J* = 17.5, 1 H, PhCH_2); 4.80 (*A* of *AB*, *J* = 17.5, 1 H, PhCH_2); 7.30–7.70 (*m*, 7 arom. H); 8.09–8.12 (*m*, 2 arom. H). ^{13}C-NMR: 38.4; 51.0; 52.4; 53.4; 64.9; 105.9; 119.8; 121.9; 122.1; 122.3; 126.5; 128.7; 129.4; 129.6; 133.4; 134.7; 142.7; 146.3; 148.5; 151.5; 164.3; 165.3. EI-MS (70 eV): 448 (23, M^+), 326 (91), 389 (73), 91 (100). Anal. calc. for $C_{23}H_{20}N_4O_6$ (448.43): C 61.60, H 4.49, N 12.49; found: C 61.45, H 4.38, N 12.40.

Dimethyl 6-Amino-1-benzyl-5-cyano-1,4-dihydro-4-(4-nitrophenyl)pyridine-2,3-dicarboxylate (**5g**). Yield 389 mg (87%). M.p. 140–142° (dec.). IR(KBr): 3428, 3344, 2953, 2187, 1744, 1688, 1654, 1626, 1574, 1425, 1347. ^{1}H-NMR: 3.64 (*s*, MeO); 3.80 (*s*, MeO); 4.24 (br. *s*, NH_2); 4.69 (*AB* (*q*), *J* = 17.5, PhCH_2); 4.70 (*s*, H–C(4)); 7.26–7.40 (*m*, 7 arom. H); 8.13 (*d*, *J* = 8.7, 2 arom. H). ^{13}C-NMR: 38.5; 51.0; 52.3; 53.3; 65.3; 106.0; 124.1; 126.7; 127.8; 128.9; 129.4; 134.7; 142.8; 147.0; 150.9; 151.4; 164.2; 165.2. EI-MS (70 eV): 402 (M^+), 326 (67), 312 (38), 91 (100), 122 (10), 69 (57). Anal. calc. for $C_{23}H_{20}N_4O_6$ (448.43): C 61.60, H 4.49, N 12.49; found: C 61.47, H 4.37, N 12.39.

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Received June 7, 2010