Reaction of 1,3-Dicarbonyl Compounds with *o*-Phenylenediamine or 3,3'-Diaminobenzidine in Water or under Solvent-free Conditions via Microwave Irradiation

Zhong-Xia Wang* and Hua-Li Qin

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China.

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Reaction of *o*-phenylenediamine with β-diketones or β-ketoesters in water formed 2-substituted benzimidazoles. Reaction of 3,3'-diaminobenzidine gave similar results. Under microwave irradiation conditions solvent-free reaction of *o*-phenylenediamine with β-ketoesters afforded 1,5-benzodiazepin-2-one derivatives. An exception is the reaction of *o*-phenylenediamine with ethyl acetoacetate under microwave irradiation, which gave 2-methylbenzimidazole.

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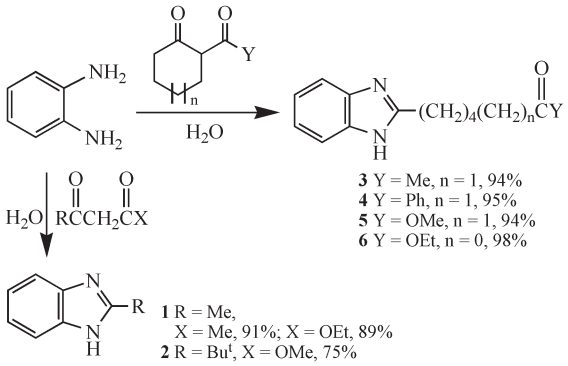
Synthesis of heterocyclic compounds in aqueous media and under solvent-free conditions using microwave irradiation has been studied extensively [1-5]. In aqueous media a number of organic reactions proceed more rapidly and efficiently than in organic solvents. Some of the reactions show also different regio- or diasteroselectivity when carried out in water instead of in the usual organic solvents [6-9]. For example, reaction of alkynes with azides in hot water yields 1,2,3-triazole derivatives regioselectively [10]. Microwave irradiation provides unique chemical processes with special attributes such as enhanced reaction rates, higher yields, greater selectivity and the ease of manipulation [5].

Benzimidazoles and 1,5-benzodiazepin-2-ones are of potential biological interest. Benzimidazoles have been widely used in medicinal chemistry [11,12]. Their synthesis was also extensively explored, including use of some green synthetic methods [13-15]. 1,5-Benzodiazepin-2-one derivatives are of pharmacological activity [16,17]. However, studies on their synthesis are relatively rare [17-21]. Here we report our investigation on reactions of 1,3-dicarbonyl compounds with *o*-phenylenediamine or 3,3'-diaminobenzidine in aqueous media or under solvent-free conditions using microwave irradiation and synthesis of benzimidazole and 1,5-benzodiazepin-2-one derivatives.

Reaction of *o*-phenylenediamine with 2,4-pentanedione or methyl pivaloylacetate in distilled water under reflux conditions afforded 2-alkylbenzimidazoles **1** and **2**, respectively (Scheme 1). Reaction of *o*-phenylenediamine with 2-acylcyclohexanones or 2-cycloalkanonecarboxylate gave benzimidazole derivatives **3**-**6** (Scheme 1) in excellent yields. The reactions are chemoselective. In each reaction only the carbonyl of the cycloalkanone acts with the amino groups of *o*-phenylenediamine. The reaction of 3,3'-diaminobenzidine with the β-diketones or β-ketoesters was similar giving compounds **7**-**10** (Scheme 2). It is noteworthy that the reaction of 3,3'-diaminobenzidine must be carried out under nitrogen. If the reaction was performed in air, a mixture was obtained. This may be because 3,3'-diaminobenzidine is more air-sensitive than

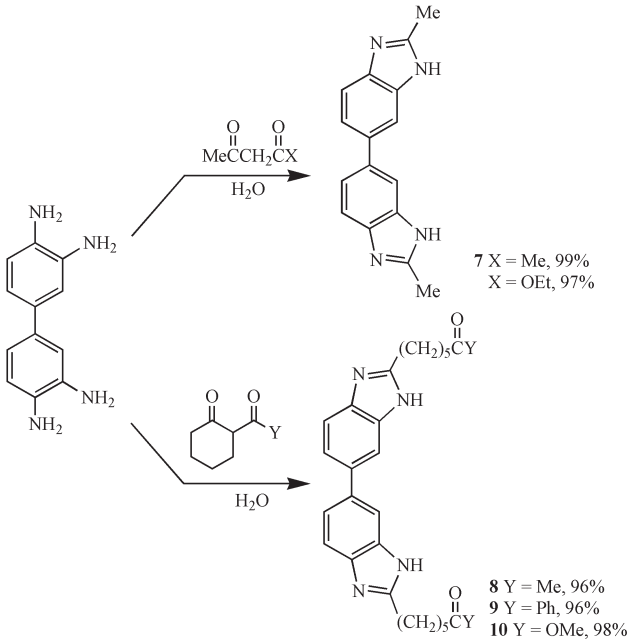
Scheme 1

Condensation of 1,3-dicarbonyl compounds and *o*-phenylenediamine in water



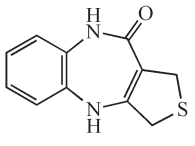
Scheme 2

Condensation of 1,3-dicarbonyl compounds and 3,3'-diaminobenzidine in water

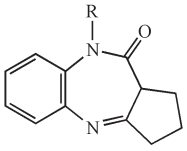


o-phenylenediamine. All products were solid and isolated by simple filtration. The products have good purity shown by their respective ^{1}H NMR spectra. However, the samples for elemental analyses and melting points determination were recrystallized from appropriate solvents (see experimental section).

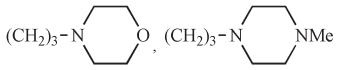
Solvent-free reaction of *o*-phenylenediamine with β-ketoesters under microwave irradiation are summerized in Scheme 3. Reaction of *o*-phenylenediamine with $RC(O)CH_2COOMe$ (R = Bu^t or Ph) afforded 1,5-benzodiazepin-2-one derivatives **11** and **12**, respectively. Similar reaction with methyl cyclohexanonecarboxylate produced corresponding 1,5-benzodiazepin-2-one derivative **13**, while with methyl cyclopentanonecarboxylate afforded compound **14**. Their ^{1}H and ^{13}C NMR spectra showed that compounds **11**-**13** exist in the imine forms, while **14** in the enamine form [22,23]. Which forms the 1,5-benzodiazepin-2-one derivatives exist in depend on the skeletal structure of the compounds and the properties of the substituted groups. For example, compounds **14** and **A** exist in the enamine forms [24], while the compound **B** exists in the imine form [25]; compound **13** exists in an imine form, while compound **C** exists in the enamine form [22]. In addition, compound **14** can also be transformed to the imine form during the reaction shown in eq. 1 [26].

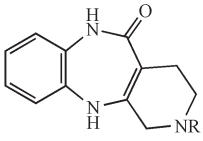


A



B R = $(CH_2)_2NMe_2$, $(CH_2)_3NMe_2$

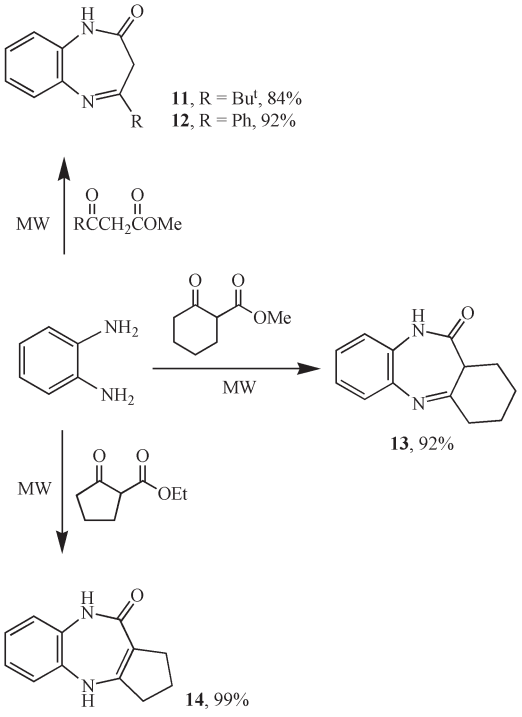


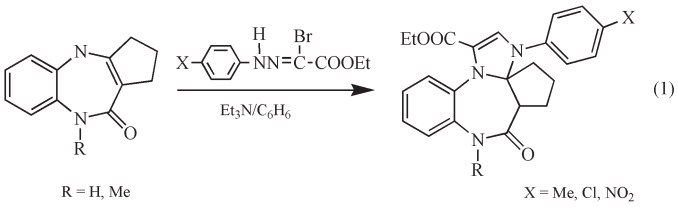


C R = Me, CH_2Ph

Scheme 3

Solvent-free reactions of *o*-phenylenediamine with β-ketoesters under microwave irradiation



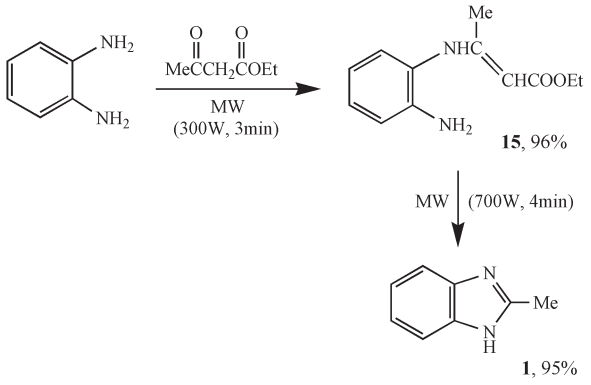


(1)

A mixture of *o*-phenylenediamine and ethyl acetoacetate was irradiated with microwave (300 W) for 3 min to form **15** (Scheme 4) in 96% yield. Compound **15** was further irradiated with microwave (700 W) for 4 min to yield 2-methylbenzimidazole in 95% yield. If a mixture of *o*-phenylenediamine and ethyl acetoacetate was irradiated with microwave (700 W) for 7 min, 2-methylbenzimidazole was obtained. Hence, compound **15** is an intermediate in the formation of 2-methylbenzimidazole from *o*-phenylenediamine and ethyl acetoacetate under microwave irradiation. The reactivity difference between ethyl acetoacetate and other β-ketoesters $RC(O)CH_2CO_2R^1$ may be caused by the steric hinderance of R groups. Soufiaoui and co-workers reported [28] that the reaction of *o*-phenylenediamine with ethyl acetoacetate in xylene under microwave irradiation gave 4-methyl-1*H*-1,5-benzodiazepin-2(3*H*)-one in 83% yield. This shows that reaction media affect the reaction significantly.

Scheme 4

Solvent-free reaction of *o*-phenylenediamine with ethyl acetoacetate under microwave irradiation



In addition, reaction of *o*-phenylenediamine with β-diketones under solvent-free conditions *via* MW radiation was also tried. However, each reaction gave a mixture.

EXPERIMENTAL

Reactions using *o*-phenylenediamine as starting material were performed in air, while reactions of 3,3'-diaminobenzidine were carried out under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker av300 or Bruker av400 spectrometer and the chemical shifts are referenced to internal solvent resonances. IR spectra were recorded on a Bruker VECTOR-22 spectrometer. MW reactions were carried out using an unmodified Sanyo EM-202ES1 household microwave oven. Elemental analyses were performed by the Analytical Center of University of Science and Technology of China.

2-Methyl-1*H*-benzimidazole (**1**).

A mixture of *o*-phenylenediamine (1.06 g, 9.80 mmol), 2,4-pentanedione (1.02 g, 10.2 mmol) and distilled water (20 ml) was refluxed for 5 h. with stirring. The mixture was cooled to room temperature and filtered. The white solid was washed with distilled water and dried in air to give **1** (1.18 g, 91%). **1** was recrystallized from EtOH, m.p. 176-177 °C (lit.[14] 177-178°C). ^{1}H NMR ($CDCl_3$): δ 2.57 (s, 3H, Me), 7.12-7.19 (m, 2H, C_6H_4), 7.44-7.50 (m, 2H, C_6H_4). IR (KBr): 3093w, 3062m, 2994m, 2906m, 2877m, 2847m, 2784m, 2719m, 2677m, 1622m, 1589w, 1556s, 1487w, 1450vs, 1421vs, 1386s, 1360m, 1271vs, 1219m, 1027m, 1003w, 896w, 834m, 737s cm^{-1}.

Similar reaction between *o*-phenylenediamine (1.06 g, 9.80 mmol) and ethyl acetoacetate (1.30 g, 9.99 mmol) afforded **1** (1.16 g, 89%).

The reactions of other β-diketones or β-ketoesters with *o*-phenylenediamine followed the same procedures and compounds **2**-**6** were obtained.

2-*t*-Butyl-1*H*-benzimidazole (**2**) [14].

Reaction between *o*-phenylenediamine (1.06 g, 9.80 mmol) and methyl 4,4-dimethyl-3-oxopentanoate (1.58 g, 9.98 mmol) in distilled water (20 ml) formed white solid product **2** (1.29 g, 75%). **2** was recrystallized from EtOH, m.p. 237.5-238.5 °C. ^{1}H NMR (DMSO-d_6): δ 1.40 (s, 9H, Bu^t), 7.10-7.12 (m, 2H, C_6H_4), 7.40 (d, *J* = 7 Hz, 1H, C_6H_4), 7.53 (d, *J* = 6.8 Hz, 1H, C_6H_4), 12.06 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 29.70, 33.61, 111.20, 118.75, 121.16, 121.86, 135.08, 143.24, 162.61. IR (KBr): 3065w, 3051w, 2967s, 2921m, 2872m, 2773m, 2677m, 1621vw, 1590vw, 1532w, 1451s, 1407vs, 1362m, 1308m, 1275s, 1219m, 1180w, 1013m, 992m, 748m, 734m cm^{-1}.

7-(1*H*-Benzo[*d*]imidazol-2-yl)heptan-2-one (**3**).

Reaction between *o*-phenylenediamine (1.06 g, 9.80 mmol) and 2-acetylcyclohexanone (1.40 g, 10.06 mmol) in distilled water (20 ml) gaved pale yellow solid **3** (2.12g, 94%). **2** was recrystallized from CH_3COOEt, m.p. 95.5-96.5°C. ^{1}H NMR ($CDCl_3$): δ 1.23-1.33 (m, 2H, CH_2), 1.45-1.55 (m, 2H, CH_2), 1.76-1.86 (m, 2H, CH_2), 2.03 (s, 3H, Me), 2.33 (t, *J* = 7 Hz, 2H, CH_2), 2.95 (t, *J* = 7.3 Hz, 2H, CH_2), 7.17-7.20 (m, 2H, C_6H_4), 7.51-7.54 (m, 2H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 22.98, 27.97, 28.26, 28.48, 29.99, 43.22, 114.50, 123.15, 136.71, 155.02, 209.29. IR (KBr): 3173m, 3123m, 3107m, 3044m, 3029m, 2934s, 2889m, 2863s, 2784m, 2636m, 2612m, 1712vs, 1623m, 1534m, 1456s, 1437m, 1412s, 1367m, 1274s, 1223w, 1158m, 1014w, 771m cm^{-1}.

Anal. Calcd. for $C_{14}H_{18}N_2O$: C, 73.01, H, 7.88, N, 12.16. Found: C, 73.14, H, 8.02, N, 12.35.

6-(1*H*-Benzo[*d*]imidazol-2-yl)-1-phenylhexan-1-one (**4**).

Reaction of *o*-phenylenediamine (1.06 g, 9.80 mmol) and 2-benzoylcyclohexanone (2.02 g, 9.89 mmol) in distilled water (20 ml) afforded pale yellow solid **4** (2.72g, 95%). **4** was recrystallized from CH_3COOEt, m.p. 140-141°C. ^{1}H NMR ($CDCl_3$): δ 1.32-1.43 (m, 2H, CH_2), 1.64-1.73 (m, 2H, CH_2), 1.74-1.86 (m, 2H, CH_2), 2.85-2.92 (m, 4H, CH_2), 7.11-7.14 (m, 2H, H_{ar}), 7.35-7.40 (m, 2H, H_{ar}), 7.46-7.50 (m, 3H, H_{ar}), 7.84-7.88 (m, 2H, H_{ar}). ^{13}C NMR ($CDCl_3$): δ 23.41, 27.98, 28.59, 28.75, 38.23, 114.75, 122.21, 127.47, 128.16, 128.73, 128.89, 132.12, 133.26, 136.97, 138.60, 155.15, 200.95. IR (KBr): 3086m, 3055s, 2943vs, 2899s, 2863s, 2769s, 2741s, 2681s, 2640s, 2525m, 1685vs, 1676vs, 1622m, 1596m, 1539m, 1503m, 1484m, 1447vs, 1423vs, 1368m, 1326s, 1271vs, 1212s, 1179w, 1025m, 749vs, 690vs cm^{-1}.

Anal. Calcd. for $C_{19}H_{20}N_2O$: C, 78.05, H, 6.89, N, 9.58. Found: C, 77.93, H, 6.76, N, 9.52.

Methyl 6-(1*H*-Benzo[*d*]imidazol-2-yl)hexanoate (**5**).

Reaction of *o*-phenylenediamine (1.06 g, 9.80 mmol) and methyl 2-oxocyclohexanecarboxylate (1.55 g, 9.92 mmol) in distilled water (20 ml) afforded pale yellow solid **5** (2.26 g, 94%). **4** was recrystallized from CH_3COOEt, m.p. 116.5-118.5°C. ^{1}H NMR ($CDCl_3$): δ 1.32-1.40 (m, 2H, CH_2), 1.56-1.65 (m, 2H, CH_2), 1.75-1.84 (m, 2H, CH_2), 2.26 (t, *J* = 7 Hz, 2H, CH_2), 2.86 (t, *J* = 7.3 Hz, 2H, CH_2), 3.60 (s, 3H, Me), 7.13-7.16 (m, 2H, C_6H_4), 7.45-7.49 (m, 2H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 24.35, 27.88, 28.60, 28.92, 33.78, 51.61, 114.72, 122.28, 138.21, 155.14, 174.40. IR (KBr): 3166w, 3089m, 3050m, 3029m, 2993m, 2938m, 2928m, 2866m, 2772m, 2647m, 1739vs, 1623m, 1592w, 15401m, 1456s, 1439s, 1419s, 1366m, 1336w, 1308w, 1273m, 1190m, 1165s, 1086w, 1018w, 999w, 748s cm^{-1}.

Anal. Calcd. for $C_{14}H_{18}N_2O_2$: C, 68.27, H, 7.37, N, 11.37. Found: C, 68.29, H, 7.35, N, 11.46.

Ethyl 5-(1*H*-Benzo[*d*]imidazol-2-yl)pentanoate (**6**)

Reaction of *o*-phenylenediamine (1.06g, 9.80mmol) and ethyl 2-oxocyclopentanecarboxylate (1.55g, 9.92mmol) in distilled water (20ml) afforded pale yellow solid **6** (2.37g, 98%). **6** was recrystallized from CH_3COOEt, m.p. 139-140°C (lit. [22] 138-140°C). ^1H NMR ($CDCl_3$): δ 1.19 (t, *J* = 7.1 Hz, 3H, Me), 1.65-1.72 (m, 2H, CH_2), 1.80-1.87 (m, 2H, CH_2), 2.32 (t, *J* = 7 Hz, 2H, CH_2), 2.89 (t, *J* = 7.2 Hz, 2H, CH_2), 4.08 (q, *J* = 7.1 Hz, 2H, CH_2), 7.13-7.17 (m, 2H, C_6H_4), 7.46-7.50 (m, 2H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 14.23, 24.34, 27.51, 28.86, 33.83, 60.54, 114.67, 122.14, 136.05, 155.09, 173.89. IR (KBr): 3087w, 3052w, 2989m, 2943m, 2916m, 2869m, 2776w, 2734w, 2662w, 1727vs, 1622w, 1540w, 1449s, 1422s, 1383m, 1320m, 1270m, 1229w, 1173s, 1028m, 931w, 860w, 748m cm^{-1}.

2,2'-Dimethyl-1*H*,1'*H*-5,5'-bibenzimidazolyl (**7**) [26].

A mixture of 3,3'-diaminobenzidine (0.26 g, 1.213 mmol), 2,4-pentanedione (0.25 g, 2.497 mmol) and distilled water (20 ml) was refluxed under nitrogen for 5 h. with stirring. The mixture was cooled to room temperature and filtered. The white solid was washed with distilled water and dried in air to give **7** (0.315 g, 99%). **7** was purified by recrystallizing from pyridine. ^1H NMR (DMSO-d_6): δ 2.50 (s, 6H, CH_3), 7.38-7.41 (m, 2H, C_6H_3), 7.48 (d, *J* = 8.3 Hz, 2H, C_6H_3), 7.64-7.65 (m, 2H, C_6H_3). ^{13}C NMR (DMSO-d_6): δ15.62, 113.09, 115.54, 121.71, 136.02, 152.68. IR (KBr): 3129m, 3062s, 2995s, 2921ws, 2851s, 2795s, 2686m, 1631m, 1593w, 1582w, 1556m, 1543w, 1452vs, 1403s, 1387s, 1352w, 1276s, 1215w, 1130w, 1023s, 986w, 948w, 846m, 797s, 759w, 740vw, 681w cm^{-1}.

Similar reaction between 3,3'-diaminobenzidine (0.26 g, 1.213 mmol) and ethyl acetoacetate (0.33 g, 2.53 mmol) formed **7** (0.31 g, 97%).

Compounds **8**-**10** were prepared similarly.

7-[2'-(6-Oxoheptyl)-1*H*,1'*H*-5,5'-bibenzimidazolyl-2-yl]heptan-2-one (**8**).

Reaction of 3,3'-diaminobenzidine (0.26 g, 1.213 mmol) with 2-acetylcyclohexanone (0.35 g, 2.50 mmol) in distilled water (20 ml) gave white solid **8** (0.54 g, 96%). **8** was recrystallized from acetone/dioxane, m.p. 101.5-102.5 °C. ^1H NMR (DMSO-d_6): δ 1.26-1.29 (m, 4H, CH_2), 1.47-1.53 (m, 4H, CH_2), 1.74-1.78 (m, 24H, CH_2), 2.05 (s, 6H, Me), 2.41 (t, *J* = 7.3 Hz, 4H, CH_2), 2.80 (t, *J* = 7.4 Hz, 4H, CH_2), 7.39-7.41 (m, 2H, C_6H_3), 7,50 (s, 2H, C_6H_3), 7.66 (s, 2H, C_6H_3), 12.22 (b, 2H, NH). ^{13}C NMR (DMSO-d_6): δ 21.63, 27.85, 28.63, 28.90, 30.11, 43.04, 121.28, 135.53, 156.12, 208.96. IR (KBr): 3187s, 3159s, 3123s, 3058s, 2957s, 2934s, 2878s, 2858s, 1702vs, 1627m, 1597w, 1539s, 1466s, 1454s, 1414s, 1366m, 1286s, 1222w, 1163m, 1086w, 1019w, 901w, 871m, 806s, 723m, 709m cm^{-1}.

Anal. Calcd. for $C_{28}H_{34}N_4O_2$: C, 73.33, H, 7.47, N, 12.22. Found: C, 73.18, H, 7.55, N, 11.98.

6-[2'-(6-Oxo-6-phenylhexyl)-1*H*,1'*H*-5,5'-bibenzimidazolyl-2-yl]-1-phenylhexan-1-one (**9**).

Reaction of 3,3'-diaminobenzidine (0.26 g, 1.213 mmol) with 2-benzoylcyclohexanone (0.51 g, 2.50 mmol) in distilled water (20 ml) gave pale yellow solid **9** (0.68 g, 96%). **8** was recrystallized from acetone/dioxane, m.p. 121.5-122.5°C. ^1H NMR (DMSO-d_6): δ 1.39-1.43 (m, 4H, CH_2), 1.65-1.70 (m, 4H, CH_2), 1.80-1.84 (m, 4H, CH_2), 2.83 (t, *J* = 6.7 Hz, 4H, CH_2), 3.05 (t, *J* = 7.0 Hz, 4H, CH_2), 7.31-7.74 (m, 12H, H_{ar}), 7.90-8.01 (m, 4H, H_{ar}), 12.23 (s, 2H, NH). ^{13}C NMR (DMSO-d_6): δ 23.55, 27.55, 28.323, 28.55, 37.82, 127.90, 128.33, 128.72, 129.02, 133.06, 136.77, 148.26, 200.11. IR (KBr): 3058s, 2933s, 2859s, 1678vs, 1627m, 1597m, 1578m, 1530m, 1482m, 1449vs, 1412s, 1280s, 1216m, 1178w, 1073w, 1024w, 1003w, 863w, 806m, 750w, 691s cm^{-1}.

Anal. Calcd. for $C_{38}H_{38}N_4O_2$: C, 78.32, H, 6.57, N, 9.61. Found: C, 78.41, H, 6.51, N, 9.72.

Methyl 6-[2'-(5-Methoxycarbonylpentyl)-1*H*,1'*H*-5,5'-bibenzimidazolyl-2-yl]hexanoate (**10**).

Reaction of 3,3'-diaminobenzidine (0.26 g, 1.213 mmol) with methyl 2-oxocyclohexanecarboxylate (0.38 g, 2.43 mmol) in distilled water (20 ml) gave pale yellow solid **10** (0.585 g, 98%). **10** was recrystallized from acetone/dioxane, m.p. 111.5-113.5°C. ^1H NMR (DMSO-d_6): δ 1.32-1.37 (m, 4H, CH_2), 1.54-1.61 (m, 4H, CH_2), 1.76-1.82 (m, 4H, CH_2), 2.30 (t, *J* = 7.3 Hz, 4H, CH_2), 2.78-2.84 (m, 4H, CH_2), 3.56 (s, 6H, Me), 7.42-7.73 (m, 6H, C_6H_3), 12.19 (s, 2H, NH). ^{13}C NMR (DMSO-d_6): δ 24.24, 27.33, 28.17, 28.49, 33.22, 51.26, 109.09, 118.32, 120.96, 135.26, 155.76, 173.46. IR (KBr): 3141s, 3043s, 2947s, 2867s, 1713vs, 1631m, 1538m, 1455vs, 1416s, 1374m, 1287s, 1205s, 1180s, 1141w, 1086w, 1037w, 975w, 862m, 814s, 733s cm^{-1}.

Anal. Calcd. for $C_{28}H_{34}N_4O_4$: C, 68.55, H, 6.99, N, 11.42. Found: C, 68.43, H, 7.01, N, 11.60.

4-*tert*-Butyl-1,3-dihydro-2*H*-1,5-benzodiazepin-2-one (**11**).

A mixture of *o*-phenylenediamine (1.06 g, 9.80 mmol) and methyl pivaloylacetate (1.60 g, 9.86 mmol) was irradiated using microwave at 700 W for 5 min. After cooling to room temperature, the pale yellow solid was washed with water and then dried in air to give **11** (1.77 g, 84%). **11** was recrystallized from EtOH, m.p. 138-139°C. ^1H NMR ($CDCl_3$): δ 1.31 (s, 9H, Bu^t), 3.19 (s, 2H, CH_2), 7.03-7.05 (m, 1H, C_6H_4), 7.15-7.20 (m, 2H, C_6H_4), 7.33-7.35 (m, 1H, C_6H_4), 8.90 (s, 1H, NH). ^{13}C NMR($CDCl_3$): δ 27.44, 38.84, 41.34, 121.71, 124.77, 125.99, 128.15, 170.95. IR (KBr): 3190vs, 3123vs, 3079vs, 2968vs, 2936s, 2892s, 1684vs, 1622s, 1573s, 1482vs, 1425s, 1363vs, 1300m, 1256s, 1227s, 1198m, 1165s, 1118m, 1078s, 1039w, 1025w, 944m, 887w, 831m, 795s, 764vs, 741s, 668m cm^{-1}.

Anal. Calcd. for $C_{13}H_{16}N_2O$: C, 72.19, H, 7.46, N, 12.95. Found: C, 72.08, H, 7.38, N, 13.01.

Compounds **12**-**14** were prepared similarly.

4-Phenyl-1,3-dihydro-2*H*-1,5-benzodiazepin-2-one (**12**).

Reaction of *o*-phenylenediamine (1.06 g, 9.80 mmol) with methyl 3-oxo-3-phenylpropanoate (1.78 g, 9.99 mmol) under MW radiation gave pale yellow solid **12** (2.13g, 92%). **12** was recrystallized from EtOH, m.p. 205-207°C (lit. [28] 206°C). ^1H NMR ($CDCl_3$): δ 3.52 (s, 2H, CH_2), 7.03-7.05 (m, 1H, H_{ar}), 7.15-7.22 (m, 2H, H_{ar}), 7.41-7.46 (m, 4H, H_{ar}), 8.03-8.07 (m, 2H, H_{ar}), 8.39 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 39.95, 121.86, 125.30, 126.61, 127.90, 128.86, 129.16, 131.18, 137.85, 140.20, 159.03, 167.63. IR (KBr): 3316vw, 3201m, 3063m, 2975w, 2911w, 1676vs, 1614m, 1568m, 1474m, 1442m, 1370m, 1311s, 1255m, 1018m, 940w, 881w, 755vs cm^{-1}.

1,2,3,4,10,11a-Hexahydro-1-*1H*-dibenzo[*b*,*e*][1,4]diazepin-11-one (**13**).

Reaction of *o*-phenylenediamine (1.06 g, 9.80 mmol) with methyl 2-oxocyclohexanecarboxylate (1.55 g, 9.92 mmol) under MW radiation gave pale yellow solid **13** (1.94 g, 92%).

13 was recrystallized from EtOH, m.p. 182-183°C (lit. [22] 182-183°C). ^{1}H NMR ($CDCl_3$): δ 2.06 (s, 2H, CH_2), 2.27 (s, 2H, CH_2), 3.66 (s, 4H, CH_2), 3.77 (s, 1H, CH), 6.62-6.68 (m, 2H, C_6H_4), 6.89-7.00 (m, 2H, C_6H_4), 9.92 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 22.34, 22.92, 23.98, 27.35, 50.75, 115.60, 118.38, 122.38, 122.48, 127.72, 129.24, 143.98, 159.13, 171.48. IR (KBr): 3461s, 3369vs, 3243s, 3065w, 3028w, 2984w, 2927s, 2843s, 1638vs, 1580vs, 1505s, 1459s, 1441vs, 1313s, 1245vs, 1191s, 1131m, 1079s, 1062m, 983w, 927w, 897vw, 826w, 777m, 743s cm^{-1}.

2,3,4,9-Tetrahydro-1*H*-benzo[*b*]cyclopenta[*e*][1,4]diazepin-10-one (**14**).

Reaction of *o*-phenylenediamine (1.06 g, 9.80 mmol) with ethyl 2-oxocyclopentanecarboxylate (1.55 g, 9.92 mmol) under MW radiation gave pale yellow solid **14** (1.94 g, 99%). **14** was recrystallized from EtOH, m.p. 185-187°C (lit. [22] 182-184°C). ^{1}H NMR ($CDCl_3$): δ 1.99-2.11 (m, 2H, CH_2), 2.48-2.54 (m, 2H, CH_2), 2.79-2.85 (m, 2H, CH_2), 5.90-5.91 (m, 1H, NH), 6.99-7.10 (m, 4H, C_6H_4), 8.57 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 22.38, 30.63, 32.18, 109.73, 109.94, 121.41, 122.04, 123.69, 128.48, 130.20, 136.05, 154.90. IR (KBr): 3373w, 3182m, 3136s, 3064s, 3025s, 2954s, 2900s, 2843s, 2769m, 2707w, 1705vs, 1649s, 1624s, 1484vs, 1393vs, 1294m, 1239m, 1188m, 1168m, 1106w, 961w, 888w, 795m, 745s, 731s, 697s, 663s cm^{-1}.

Ethyl (2*E*)-3-[(2-Aminophenyl)amino]but-2-enoate (**15**).

A mixture of *o*-phenylenediamine (1.06 g, 9.80 mmol) and ethyl acetoacetate (1.30 g, 9.99 mmol) was irradiated using microwave at 300 W for 3 min. After cooling to room temperature, the pale yellow solid was washed with water and then dried in air to afford **15** (2.08 g, 96%). **15** was recrystallized from hexane, m.p. 58-61°C (lit. [29] 59-62°C). ^{1}H NMR ($CDCl_3$): δ 1.22 (t, J = 7.1 Hz, 3H, Me), 1.73 (s, 3H, Me), 3.75 (s, 2H, NH_2), 4.08 (q, J = 7.1 Hz, 2H, CH_2), 4.65 (s, 1H, CH), 6.61-6.69 (m, 2H, C_6H_4), 6.91 (d, J = 7.6 Hz, 1H, C_6H_4), 6.97-7.03 (m, 1H, C_6H_4), 9.63 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 14.89, 19.78, 58.88, 85.24, 114.53, 116.88, 120.39, 122.18, 138.77, 151.74, 161.76, 170.86. IR (KBr): 3451m, 3356m, 3246w, 3183vw, 3067w, 2984m, 2920w, 2872w, 2850w, 2789w, 2727w, 2679w, 1648vs, 1622vs, 1597vs, 1511m, 1485s, 1451m, 1434m, 1385m, 1360m, 1271vs, 1219m, 1169vs, 1057s, 1025s, 983w, 834w, 785s, 753s, 737s cm^{-1}.

Transformation of **15** to 2-Methyl-1*H*-benzimidazole (**1**) *via* MW radiation.

Ethyl (2*E*)-3-[(2-aminophenyl)amino]but-2-enoate (**15**) (1.0 g, 4.54 mmol) was irradiated using microwave at 700 W for 4 min. After cooling to room temperature, the solid was washed with water and then dried in air to give white solid **1** (0.57g, 95%).

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REFERENCES AND NOTES

[1] C.-J. Li, *Chem. Rev.*, **93**, 2023 (1993).
[2] G. Molteni, A. Ponti and M. Orlandi, *New J. Chem.*, **26**, 1340 (2002).
[3] G. Broggini, G. Molteni and G. Zecchi, *Heterocycles*, **47**, 541 (1998).
[4] A. de la Hoz, A. Díaz-Ortis, A. Moreno and F. Lauga, *Eur. J. Org. Chem.*, 3659 (2000).
[5] Y. Xu and Q.-X. Guo, *Heterocycles*, **63**, 903 (2004).
[6] J. W. Wijnen, S. Zavarise and J. B. F. N. Engberts, *J. Org. Chem.*, **61**, 2001 (1996).
[7] S. Otto, W. Blokzijl and J. B. F. N. Engberts, *J. Org. Chem.*, **59**, 5372 (1994).
[8] U. M. Lindström, *Chem. Rev*., **102**, 2751 (2002).
[9] J. F. Blake, D. Lim and W. L. Jorgensen, *J. Org. Chem*., **59**, 803 (1994).
[10] Z.-X. Wang and H.-L. Qin, *Chem.Commun.*, 2450 (2003).
[11] G. V. Reddy, V. V. V. N. S. R. Rao, B. Narsaiah and P. S. Rao, *Synth. Commun.*, **32**, 2467 (2002), and references therein.
[12] M. P. Singh, S. Sasmal, W. Lu and M. N. Chatterjee, *Synthesis*, 1380 (2000).
[13] P. N. Preston, *Chem. Rev.*, **74**, 279 (1974).
[14] L. M. Dudd, E. Venardou, E. Garcia-Verdugo, P. Licence, A. J. Blake, C. Wilson and M. Poliakoff, *Green Chem.*, **5**, 187 (2003).
[15] C. T. Brain and J. T. Steer, *J. Org. Chem.*, **68**, 6814 (2003).
[16] H. Abdel-Ghany, A. M. El-Sayed, A. Khodairy and H. Salah, *Synth. Commun.*, **31**, 2523 (2001).
[17] M. H. Rao, A. P. R. Reddy and V. Veeranagaiah, *Synthesis*, 446 (1992).
[18] M. Hamdi, O. Grech, R. Sakellariou and V. Spéziale, *J. Heterocyclic Chem.*, **31**, 509 (1994).
[19] T.-H. Chuang and K. B. Sharpless, *Org. Lett*., **2**, 3555 (2000).
[20] M. J. Fray, K. Cooper, M. J. Parry, K. Richardson and J. Steelet, *J. Med. Chem*., **38**, 3514 (1995).
[21] R. Achour, M. Z. Cherkaoui, E. M. Essassi and R. Zniber, *Synth. Commun.*, **24**, 2899 (1994).
[22] A. Rossi, A. Hunger, J. Kebrle and K. Hoffmann, *Helv. Chim. Acta*, **43**, 1298 (1960).
[23] A. Rossi, A. Hunger, J. Kebrle and K. Hoffmann, *Helv. Chim. Acta*, **43**, 1046 (1960).
[24] J. B. Press, C. M. Hofmann, N. H. Eudy, W. J. Fanshawe, I. P. Day, E. N. Greenblatt, S. R. Safir, *J. Med. Chem.*, **22**, 725 (1979).
[25] A. Mule, G. Pirisino, M. D. Moretti, F. Savelli, A. Boido, M. Satta, A. Peana, *Boll. Chim. Farm.*, **133**, 167 (1994).
[26] A. Aatif, A. Baouid, A. Benharref, A. Hasnaoui, *Synth. Commun.*, **30**, 2647 (2000).
[27] J. Schoenleber, P. L. et J. Néel, *Bull. Soc. Chim. Fr.*, 1926 (1969).
[28] K. Bougrin, A. K. Bennani, S. F. Tétouani and M. Soufiaoui, *Tetrahedron Lett.*, **35**, 8373 (1994).
[29] W. A. Sexton, *J. Chem. Soc.*, 303 (1942).