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Microwave-Promoted Beller's Synthesis of Substituted Phthalates

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Abstract: A rapid and efficient synthesis of substituted phthalates via microwave-promoted Beller's reaction of aldehydes, amides, and dimethyl acetylenedicarboxylate is described. This one-pot, multicomponent reaction was performed under acetic anhydride–free and solvent-free conditions.

Keywords: Beller's reaction, microwave, multicomponent reactions, phthalates

In the past decade, multicomponent reactions (MCRs) have emerged as a powerful tool for the creation of molecular complexity and diversity through facile formation of several new covalent bonds in one-pot transformations.[1] This methodology offers significant advantages over the stepwise procedures and therefore possesses high efficiency in the synthesis of complex organic building blocks from easily available starting materials.[2] Recently, Beller and coworkers developed a multicomponent reaction of amides, aldehyde, and dienophile (AAD reaction) for the straightforward synthesis of highly substituted cyclohexenes[3] and anilines.[4] This AAD reaction also provides an efficient strategy for the synthesis of alkyl phthalates.[5] However, their synthesis of phthalates usually requires long reaction times (24–64 h) and stoichiometric amounts of acetic anhydride.

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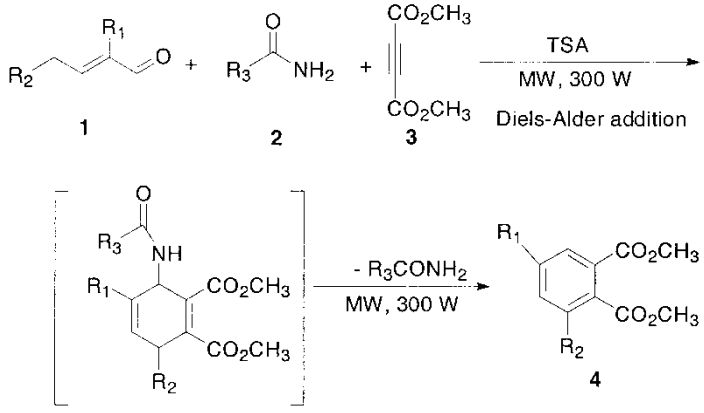
In connection with our research on microwave-promoted MCRs,[6] herein we report a microwave-promoted Beller's reaction of amides, aldehydes, and electron-deficient alkynes, which led to a rapid and efficient synthesis of alkyl phthalates under acetic anhydride–free and solvent-free conditions.

Our work began with the investigation of Beller's reaction using microwave irradiation instead of conventional heating (Scheme 1). Initially, equal equivalents of *trans*-octenal (**1a**), acetamide (**2a**), and dimethyl acetylenedicarboxylate (**3**) and catalytic amounts of *p*-toluenesulfonic acid (TSA) were used. The mixture was irradiated in a microwave at 300 W to result in dimethyl phthalate **4a**, and the yield was almost quantitative. We then examined the possibility for using catalytic amounts of the amide that is eliminated in the last step of the domino reaction as shown in Scheme 1. It was found that the reaction of α,β-unsaturated aldehydes **1** and dimethyl acetylene-dicarboxylate (**3**) with amides **2** (5 mol%) in the presence of TSA (1.5 mol%) at 300 W for 10 min obtained phthalate derivatives **4** in excellent yields (93–98%) (Table 1). The reactions were performed under solvent-free and acetic anhydride–free conditions, which are necessary for Beller's procedure.[3–5]

We also employed the saturated aldehydes **5** instead of α,β-unsaturated aldehydes **1** for the Beller's reaction. The in situ generated α,β-unsaturated aldehydes from **5** under the microwave reaction conditions could also afford substituted phthalate derivatives **6** (Scheme 2). Eleven aliphatic aldehydes (Table 2, entries 1–11, 13, and 14) and phenylacetaldehyde (Table 2, entries 12 and 15) were tested. It was found that all of the reactions gave good to excellent yields (80–98%). Additionally, acetamide (Table 2, entries 3, 5, and 12) is almost as effective as benzamide (Table 2, entries 13–15).



Scheme 1.

Table 1. Synthesis of substituted phthalates 4

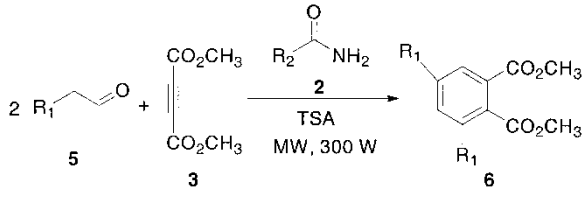
Entry	R_1	R_2	R_3	Product	Isolated yield (%)
1	H	n-C_4H_9	CH_3	**4a**	96
2	H	n-C_4H_9	Ph	**4a**	95
3	H	H	CH_3	**4b**	98
4	CH_3	$(CH_3)_2C{=}CHCH_2$	CH_3	**4c**	94
5	CH_3	$(CH_3)_2C{=}CHCH_2$	Ph	**4c**	93

This domino reaction involves the intermediates of an acetamido butadiene or benzamido butadiene species that undergoes Diels–Alder addition to dimethyl acetylenedicarboxylate. The resultant acetamidodiene or benzamidodiene is subjected to elimination of acetamide or benzamide under microwave irradiation conditions to give substituted dimethyl phthalates.

In summary, we have developed an efficient synthesis of substituted phthalates via microwave-promoted Beller's multicomponent reaction of aldehydes, amides, and dimethyl acetylenedicarboxylate. As compared with the Beller's method,[5] this one-pot procedure is rapid and can be performed in the absence of acetic anhydride and under solvent-free conditions. It is noteworthy that the in situ generated α,β-unsaturated aldehydes under the reaction conditions could also react to give the corresponding phthalate derivatives. The domino condensation–cycloaddition–elimination sequence has been applied to a variety of aldehydes.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 983 FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Advance DMX 500 instrument. HRMS data were obtained on a Bruker FT-ICR-MS Apex III apparatus. MS data were recorded on a Bruker Esquir 3000-plus instrument. HPLC analysis was carried out on Agilent 1100 (250 × 4.6-mm C18 column, gradient elution 80% MeOH and 20% H_2O, 0.8 mL/min, UV detection at λ 254 nm).



Scheme 2.

Table 2. Synthesis of substituted phthalates **6**

Entry	R_1	R_2	Product	Isolated yield (%)
1	H	CH_3	**6a**	85
2	CH_3	CH_3	**6b**	93
3	C_2H_5	CH_3	**6c**	96
4	*n*-C_3H_7	CH_3	**6d**	95
5	*i*-C_3H_7	CH_3	**6e**	83
6	*n*-C_4H_9	CH_3	**6f**	91
7	*n*-C_5H_{11}	CH_3	**6g**	90
8	*n*-C_6H_{13}	CH_3	**6h**	89
9	*n*-C_7H_{15}	CH_3	**6i**	93
10	*n*-C_8H_{17}	CH_3	**6j**	95
11	*n*-$C_{10}H_{21}$	CH_3	**6k**	95
12	Ph	CH_3	**6l**	98
13	C_2H_5	Ph	**6c**	91
14	*i*-C_3H_7	Ph	**6e**	80
15	Ph	Ph	**6l**	95

General Procedure for the Synthesis of Substituted Phthalates 4 from α,β-Unsaturated Aldehydes 1

Acetamide (13.2 mg, 5 mol%), α,β-unsaturated aldehydes (2.5 mmol), dimethyl acetylenedicarboxylate (853 mg, 5 mmol), and *p*-toluenesulfonic acid (22 mg, 1.5 mol%) were combined in a 5 mL glass bottle immersed in a Pyrex® crystallization dish filled with neutral alumina (500 g, 100–200 mesh). This setup was placed at the cavity of microwave synthesizer and irradiated at 300 W for 10 min. The reaction mixture was cooled to room temperature and then dissolved in ethyl acetate (50 mL). The solution was washed with water, dried over anhydrous Na_2SO_4, and evaporated in vacuum. The crude products were purified by a flash-column chromatography on silica gel with ethyl acetate–hexane (1 : 10, v/v) as eluent.

***Compound* 4a:** Light yellow oil; IR (neat) 1732, 1592, 1460, 1433, 1283, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, $J = 7.6$ Hz, 1 H), 7.43 (m, 2 H), 3.94 (s, 3 H), 3.89 (s, 3 H), 2.62 (t, $J = 7.80$ Hz, 2 H), 1.59–1.57 (m, 2 H), 1.37–1.35 (m, 2 H), 0.94 (t, $J = 7.4$ Hz, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 166.6, 140.7, 135.2, 134.0, 129.3, 128.0, 127.8, 52.7, 52.6, 33.6, 33.2, 22.7, 14.1 ppm; MS (ESI) m/z 273 ($[M + Na]^+$); HRMS (ESI) calcd. for $C_{14}H_{18}O_4Na$ $(M + Na)^+$ 273.1097, found 273.1098.

***Compound* 4b:** Light yellow oil; IR (neat) 1733, 1593, 1460, 1433, 1285, 1253, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.72–7.71 (d, $J = 7.5$ Hz, 2 H), 7.53–7.52 (d, $J = 7.5$ Hz, 2 H), 3.89 (s, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 132.1, 131.3, 129.1, 52.82 ppm; MS (ESI) m/z

217 ($[M + Na]^+$); HRMS (ESI): calcd. for $C_{10}H_{10}O_4Na$ $(M + Na)^+$ 217.0471, found 217.0467.

***Compound* 4c:** Light yellow oil; IR (neat) 1733, 1592, 1460, 1433, 1286, 1254, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, $J = 7.2$ Hz, 1 H), 7.22 (d, $J = 7.2$ Hz, 1 H), 5.18 (t, $J = 5.2$ Hz, 1 H), 3.90 (s, 3 H), 3.88 (s, 3 H), 2.70 (d, $J = 4.9$ Hz, 2 H), 2.35 (s, 3 H), 1.55 (s, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 167.8, 146.5, 136.5, 133.1, 132.8, 130.0, 128.9, 126.7, 118.5, 52.7, 52.6, 25.8, 20.2, 19.2, 17.8 ppm; MS (ESI) m/z 299 ($[M + Na]^+$). HRMS (ESI): calcd. for $C_{16}H_{20}O_4Na$ $(M + Na)^+$ 299.1254, found 299.1242.

General Procedure for the Synthesis of Substituted Phthalates 6 from Aldehydes 5

Acetamide (13.2 mg, 5 mol%), aldehydes (5 mmol), dimethyl acetylenedicarboxylate (853 mg, 5 mmol), and *p*-toluenesulfonic acid (22 mg, 1.5 mol%) were combined in a 5 mL glass bottle immersed in a Pyrex® crystallization dish filled with neutral alumina (500 g, 100–200 mesh). This setup was placed at the cavity of microwave synthesizer and irradiated at 300 W for 10 min. The reaction mixture was cooled to room temperature and then dissolved in ethyl acetate 50 mL. The solution was washed with water, dried over anhydrous Na_2SO_4, and evaporated in vacuum. The crude products were purified by a flash-column chromatography on silica gel with ethyl acetate–hexane (1 : 10, v/v) as eluent.

***Compound* 6a:** Light yellow oil; IR (neat) 1733, 1593, 1460, 1433, 1285, 1253, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.72–7.71 (d, $J = 7.5$ Hz, 2 H), 7.53–7.52 (d, $J = 7.5$ Hz, 2 H), 3.89 (s, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 132.1, 131.3, 129.1, 52.82 ppm; MS (ESI) m/z 217 ($[M + Na]^+$); HRMS (ESI): cald. for $C_{10}H_{10}O_4Na$ $(M + Na)^+$ 217.0471, found 217.0467.

***Compound* 6b:** Light yellow oil; IR (neat) 1733, 1592, 1460, 1434, 1283, 1253, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.60 (s, 1 H), 7.18 (s, 1 H), 3.89 (s, 3 H), 3.85 (s, 3 H), 2.32 (s, 3 H), 2.29 (s, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 166.7, 139.3, 135.6, 135.2, 132.6, 128.0, 52.5, 21.1, 19.1 ppm; MS (ESI) m/z 245 ($[M + Na]^+$); HRMS (ESI): calcd. for $C_{12}H_{14}O_4Na$ $(M + Na)^+$ 245.0784, found 245.0785.

***Compound* 6c:** Light yellow oil; IR (neat) 1732, 1607, 1459, 1435, 1287, 1253, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.65 (s, 1 H), 7.25 (s, 1 H), 3.91 (s, 3 H), 3.87 (s, 3 H), 2.67–2.61 (m, 4 H), 1.27–1.25 (m, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 166.8, 145.9, 142.0, 132.8, 132.4, 128.2, 127.2, 52.58, 52.58, 28.8, 26.6, 15.8, 15.5 ppm; MS (ESI): m/z 273

($[M + Na]^+$); HRMS (ESI): calcd. for $C_{14}H_{18}O_4Na$ $(M + Na)^+$ 273.1097, found 273.1097.

***Compound* 6d:** Light yellow oil; IR (neat) 1730, 1594, 1460, 1433, 1283, 1254, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.65 (s, 1 H), 7.27 (s, 1 H), 3.92 (s, 3 H), 3.87 (s, 3 H), 2.62–2.56 (m, 4 H), 1.67–1.62 (m, 4 H), 0.96–0.92 (m, 6 H) ppm; ^{13}C NMR (125 MHZ, $CDCl_3$): δ 170.3, 166.9, 144.1, 140.4, 134.1, 132.7, 128.2, 127.9, 52.6, 37.8, 35.5, 24.7, 24.5, 14.2, 13.9 ppm; MS (ESI): m/z 301 ($[M + Na]^+$); HRMS (ESI): calcd. for $C_{16}H_{22}O_4Na$ $(M + Na)^+$ 301.1410, found 301.1403.

***Compound* 6e:** Light yellow oil; IR (neat) 1731, 1592, 1460, 1433, 1284, 1253, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.70 (s, 1 H), 7.37 (s, 1 H), 3.92 (s, 3 H), 3.87 (s, 3 H), 2.97–2.93 (m, 2 H), 1.26–1.24 (m, 12 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 166.8, 150.5, 146.4, 132.2, 128.4, 127.8, 125.9, 52.6, 52.5, 34.3, 31.1, 24.2, 23.9 ppm; MS (ESI): m/z 301 ($[M + Na]^+$); HRMS (ESI): calcd. for $C_{16}H_{22}O_4Na$ $(M + Na)^+$ 301.1410, found 301.1404.

***Compound* 6f:** Light yellow oil; IR (neat) 1732, 1607, 1463, 1435, 1294, 1269, 1210 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1 H), 7.22 (s, 1 H), 3.91 (s, 3 H), 3.87 (s, 3 H), 2.64–2.58 (m, 4 H), 1.61–1.58 (m, 4 H), 1.37–1.32 (m, 4 H), 0.94–0.90 (m, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 166.8, 144.4, 140.7, 133.9, 132.5, 128.2, 127.8, 52.6, 35.5, 33.7, 33.5, 33.1, 22.8, 22.5, 14.1 ppm; MS (ESI): m/z 307 ($[M + H]^+$). HRMS (ESI): calcd. for $C_{18}H_{26}O_4Na$ $(M + Na)^+$ 329.1723, found 329.1715.

***Compound* 6g:** Light yellow oil; IR (neat) 1733, 1607, 1464, 1435, 1279, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1 H), 7.22 (s, 1 H), 3.91 (s, 3 H), 3.87 (s, 3 H), 2.63–2.56 (m, 4 H), 1.61–1.59 (m, 4 H), 1.33–1.29 (m, 8 H), 0.90–0.87 (m, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 166.8, 144.3, 140.7, 133.9, 132.5, 128.2, 127.7, 52.5, 52.4, 35.7, 33.4, 31.8, 31.5, 31.2, 31.0, 22.7, 22.6, 14.2, 14.1 ppm; MS (ESI): m/z 357 ($[M + Na]^+$). HRMS (ESI): calcd. for $C_{20}H_{30}O_4Na$ $(M + Na)^+$ 357.2036, found 357.2040.

***Compound* 6h:** Light yellow oil; IR (neat) 1734, 1592, 1460, 1433, 1283, 1253, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1 H), 7.22 (s, 1 H), 3.91 (s, 3 H), 3.87 (s, 3 H), 2.63–2.56 (m, 4 H), 1.60–1.57 (m, 4 H), 1.30–1.26 (m, 12 H), 0.90–0.87 (m, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 166.9, 144.4, 140.7, 133.9, 132.5, 128.2, 127.7, 52.6, 52.5, 35.8, 33.5, 32.0, 31.97, 31.6, 31.4, 29.9, 29.3, 29.2, 22.9, 14.3 ppm; MS (ESI): m/z 385 ($[M + Na]^+$). HRMS (ESI): calcd. for $C_{22}H_{34}O_4Na$ $(M + Na)^+$ 385.2339, found 385.2342.

***Compound* 6i:** Light yellow oil; IR (neat) 1732, 1594, 1460, 1433, 1284, 1256, 1208 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1 H), 7.22 (s, 1 H), 3.91 (s, 3 H), 3.87 (s, 3 H), 2.63–2.56 (m, 4 H), 1.60–1.57 (m, 4 H),

1.30–1.27 (m, 16 H), 0.89–0.87 (m, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 166.9, 144.4, 140.7, 133.9, 132.5, 128.2, 127.6, 52.5, 52.4, 35.7, 33.5, 32.0, 31.96, 31.6, 31.4, 29.6, 29.3, 29.2, 22.9, 14.3 ppm; MS (ESI): m/z 413 ($[M + Na]^+$). HRMS (ESI): calcd. for $C_{24}H_{38}O_4Na$ $(M + Na)^+$ 413.2662, found 413.2646.

***Compound* 6j:** Light yellow oil; IR (neat) 1733, 1592, 1460, 1433, 1283, 1253, 1208 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1 H), 7.22 (s, 1 H), 3.91 (s, 3 H), 3.87 (s, 3 H), 2.63–2.56 (m, 4 H), 1.60–1.57 (m, 4 H), 1.30–1.26 (m, 20 H), 0.90–0.87 (m, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 166.9, 144.3, 140.7, 133.9, 132.5, 128.2, 127.7, 52.6, 52.5, 35.8, 33.5, 32.1, 31.6, 31.4, 29.7, 29.6, 29.5, 29.4, 29.3, 22.9, 14.3 ppm; MS (ESI): m/z 441 ($[M + Na]^+$). HRMS (ESI): calcd. for $C_{26}H_{42}O_4Na$ $(M + Na)^+$ 441.2962, found 441.2960.

***Compound* 6k:** Light yellow oil; IR (neat) 1735, 1607, 1464, 1435, 1272, 1208 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1 H), 7.21 (s, 1 H), 3.91 (s, 3 H), 3.87 (s, 3 H), 2.64–2.57 (m, 4 H), 1.60–1.59 (m, 4 H), 1.30–1.26 (m, 28 H), 0.89–0.87 (m, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 166.9, 144.4, 140.7, 133.9, 132.5, 128.2, 127.7, 52.6, 52.5, 35.8, 33.5, 32.1, 31.5, 31.4, 29.9, 29.8, 29.7, 29.66, 29.62, 29.5, 29.4, 22.9, 14.3 ppm; MS (ESI): m/z 497 ($[M + Na]^+$). HRMS (ESI): calcd. for $C_{30}H_{50}O_4Na$ $(M + Na)^+$ 497.3585, found 497.3590.

***Compound* 6l:** Light yellow oil; IR (neat) 1731, 1599, 1497, 1433, 1270, 1244, 1200 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (s, 1 H), 7.79 (s, 1 H), 7.67–7.65 (m, 2 H), 7.50–7.47 (m, 2 H), 7.44–7.40 (m, 6 H), 3.96 (s, 3 H), 3.70 (s, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.5, 166.5, 142.5, 141.5, 139.6, 139.3, 133.6, 132.9, 129.3, 129.2, 129.1, 128.9, 128.8, 128.6, 128.58, 128.54, 128.2, 127.7, 127.5, 52.9, 52.5 ppm; MS (ESI): m/z 369 ($[M + Na]^+$). HRMS (ESI): calcd. for $C_{22}H_{18}O_4Na(M + Na)^+$ 369.1097, found 369.1083.

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