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Highly Selective Synthesis of 1-Phenylpentane-1, 4-Diones, and (*E*)-5-Hydroxy-5-phenylpent-3-en-2-ones Catalyzed by Organophosphorus Compounds

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ABSTRACT: *1-Phenylpentane-1, 4-diones, and (E)-5-hydroxy-5-phenylpent-3-en-2-ones were synthesized via organophosphine-catalyzed addition reaction of but-3-en-2-one with aldehydes. The features of the present protocols include high selectivity, operational simplicity, atom economy, and mild reaction conditions without transition metals.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 20:425–430, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20568

INTRODUCTION

Organocatalytic C—C bond formation is one of the most useful protocols to construct C—C bonds in organic synthesis [1]. There are many reports about the application of organophosphine up to now, but the organophosphine-catalyzed additional reactions between unsaturated C—C bonds and aldehydes remains challenging [2,3]. As such process is of great importance because of the advantages such as highly atomic economy, requiring no precious transition metal, and simple implementation of the experiment [4]. Herein, we report first organophosphorus-controlled selectively form of 1-phenylpentane-1, 4-diones [6], and (*E*)-5-hydroxy-5-phenylpent-3-en-2-ones from aromatic aldehydes and but-3-en-2-one in the presence of a catalytic amount of triphenylphosphine and tris(4-methoxylphenyl)phosphine, respectively, in one step [7] (Scheme 1).

RESULTS AND DISCUSSION

At the beginning, the reaction between but-3-en-2-one **1** and 4-nitrobenzaldehyde **2a** was used as a model to investigate the efficiency of varied catalysts. The results are described in Table 1. Various nitrogen-containing organocatalysts, such as DABCO, Et_3N, pyridine, and DBU failed to give the desired products (Table 1, entries 2, 3, 5, and 6). On the other hand, phosphorus-based catalysts could induce the reaction to give the adduct **3a** or **4a** (Table 1, entries 1, 4, and 7). It is meaningful to find that the production of **3a** or **4a** can be selectively controlled by the catalysts: Triphenylphosphine resulted in **4a** as the major product (Table 1, entry 1), whereas the relatively electron-rich catalyst tris(4-methoxyphenyl)phosphine gave **3a** as the major product (Table 1, entry 7). To our best knowledge, this is the first observation

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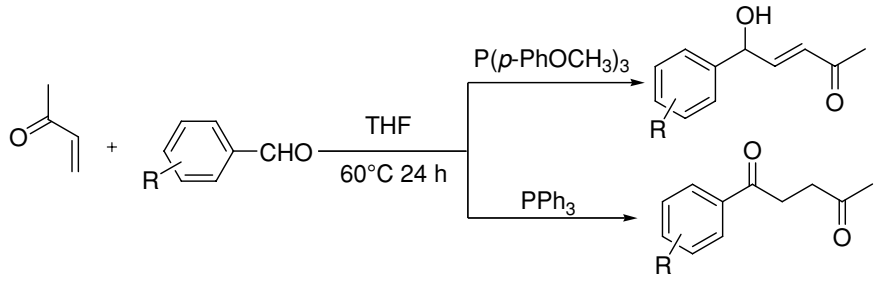
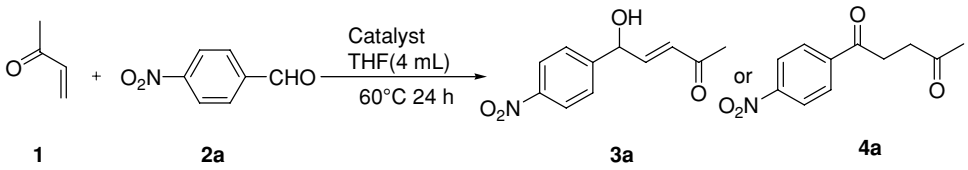


SCHEME 1

TABLE 1 Reaction of But-3-en-2-one **1** (1.0 equiv) with 4-Nitrobenzaldehyde **2a** (1.0 equiv) in the Presence of 0.2 equiv of Catalyst



1 **2a** **3a** **4a**

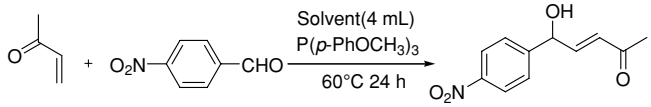
Entry	*Catalyst*	*Yield (%)*[a]
1	PPh_3	**3a:** 5, **4a:** 68
2	DABCO	None
3	Py	None
4	PBu_3	**3a:** 35, **4a:** 45
5	Et_3N	None
6	DBU	None
7	$P(p\text{-}PhOCH_3)_3$	**3a:** 73, **4a:** 11

[a]GC yields.

of different phosphorus catalysts giving different addition products from the same set of substrates/reagents in the same solvent. Moreover, the tris(4-methoxylphenyl)phosphine-catalyzed reactions of vinyl ketones or ketoesters with alkyl or aryl aldehydes to afford (*E*)-5-hydroxy-5-(alkyl or aryl)pent-3-en-2-ones have not been reported previously.

Next, the effect of various solvents on the reaction was examined to improve the yield of **3a** by using tris(4-methoxylphenyl)phosphine as the catalyst (Table 2, entries 1–6). We found THF was most suitable for this transformation (Table 2, entry 1), and increasing the reaction time from 12 to 24 h resulted in an increased GC yield (Table 1, entries 1 vs. 7) as well as increasing the catalyst loading from 0.1 equiv to 0.2 equiv (Table 1, entries 1 vs. 9); neither the extension of reaction time from 24 to 30 h (Table 1, entries 1 vs. 8) nor increasing the catalyst loading from 0.2 equiv to 0.5 equiv influenced the yield (Table 1, entries 1 vs. 10). Thus, the optimized

TABLE 2 Condition Optimization for the Reaction of But-3-en-2-one **1** (1.0 equiv) with 4-Nitrobenzaldehyde **2a** (1.0 equiv) in the Presence of 0.2 equiv of $P(p\text{-}PhOCH_3)_3$

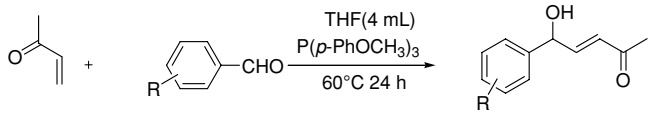


1 **2a** **3a**

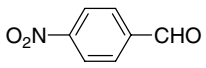
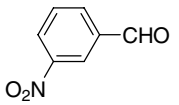
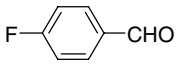
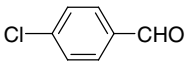
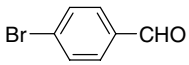
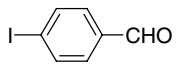
Entry	*Solvent*	*Time (h)*	*Yield of **3a***[a]
1	THF	24	73
2	$CHCl_3$	24	61
3	Toluene	24	55
4	Cyclohexane	24	37
5	DMF	24	Complex
6	CH_3CN	24	Complex
7	THF	12	57
8	THF	30	74
9[b]	THF	24	31
10[c]	THF	24	73

[a]GC yields.
[b]0.1 equiv of $P(p\text{-}PhOCH_3)_3$.
[c]0.5 equiv of $P(p\text{-}PhOCH_3)_3$.

TABLE 3 Scope of the Reaction of But-3-en-2-one **1** (1.0 equiv) with Aldehyde **2** (1.0 equiv) in the Presence of 0.2 equiv of P(*p*-PhOCH$_3$)$_3$

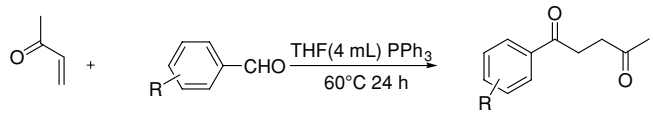


1 **2** **3**

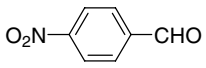
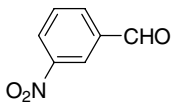
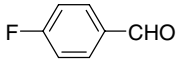
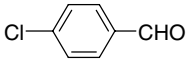
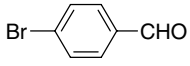
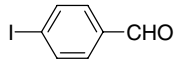
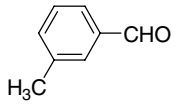
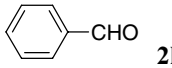
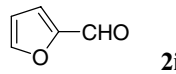
Entry	*Aryl Aldehyde*	*Yield of 3*[a]
1	 **2a**	70 (**3a**)
2	 **2b**	65 (**3b**)
3	 **2c**	55 (**3c**)
4	 **2d**	57 (**3d**)
5	 **2e**	57 (**3e**)
6	 **2f**	62 (**3f**)

[a]Isolated yield.

TABLE 4 Scope of the Reaction of But-3-en-2-one **1** (1.0 equiv) with Aldehyde **2** (1.0 equiv) in the Presence of 0.2 equiv of PPh$_3$



1 **2** **4**

Entry	*Aryl Aldehyde*	*Yield of 4*[a]
1	 **2a**	67 (**4a**)
2	 **2b**	64 (**4b**)
3	 **2c**	51 (**4c**)
4	 **2d**	49 (**4d**)
5	 **2e**	58 (**4e**)
6	 **2f**	63 (**4f**)
7	 **2g**	43 (**4g**)
8	 **2h**	50 (**4h**)
9	 **2i**	52 (**4i**)

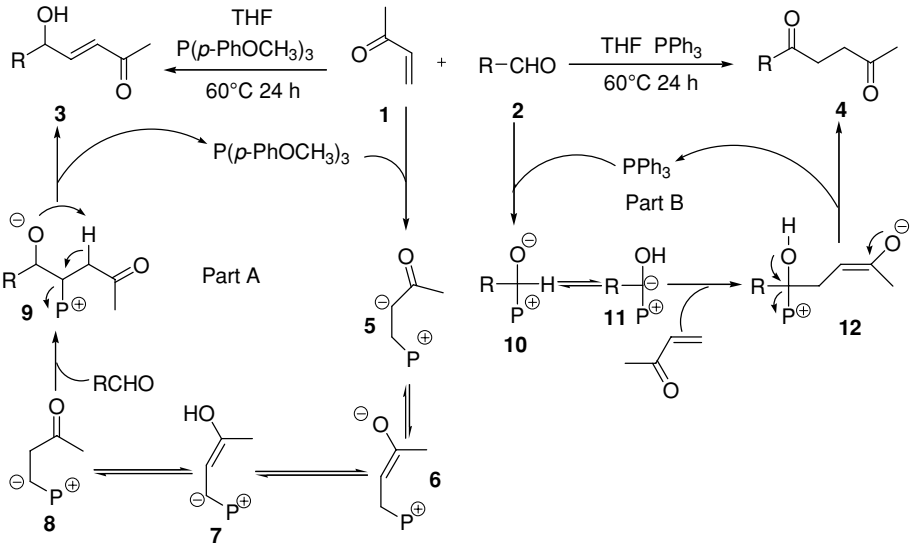
[a]Isolated yield.

reaction conditions could be established as follows: 0.2 equiv of tris(4-methoxylphenyl)phosphine catalyst with THF as the solvent at 60°C for 24 h.

With the optimized conditions in hand, several other aryl aldehydes were then examined in the reaction with but-3-en-2-one (Table 3, entries 1–6). As evident from the results, all the reactions proceeded smoothly and provided the corresponding products (*E*)-5-hydroxy-5-(R-phenyl)pent-3-en-2-ones **3**. It is noteworthy that aryl aldehydes with an electron-withdrawing group (Table 3, entries 1–2) favor the reaction compared with the electron-donating group substituted aryl aldehydes (Table 3, entries 3–6). When triphenylphosphine was used as the catalyst for the reaction under the same conditions, the isolated major products were 1-(R-phenyl)pentane-1,4-diones as described in Table 4 (Table 4, entries 1–9).

It is a very interesting phenomenon, as revealed in Tables 3 and 4 that the additions are highly selective. When tris(4-methoxylphenyl)phosphine was used as the catalyst in the reaction, 1,2-addition of but-3-en-2-one **1** toward aryl aldehydes **2** occurred predominantly and (*E*)-5-hydroxy-5-(substituted-phenyl)pent-3-en-2-ones **3** were produced (Table 3, entries 1–6), whereas replaced tris(4-methoxylphenyl)phosphine with triphenylphosphine as the catalyst in the same conditions, 1,4-addition occurred predominantly, namely, aryl aldehydes **2** added to but-3-en-2-one **1**, and provided new adducts of 1-(substituted-phenyl)pentane-1,4-diones (Table 4, entries 1–9).

We speculate the mechanism of the reaction in Scheme 2 on the basis of earlier reports [8] and our investigations. The main reason for the selectivity is that the two different phosphines attack different molecules. When P(*p*-PhOCH$_3$)$_3$ was employed, it attacks the C—C double bond of but-3-en-2-one **1** and gave the 1,2-addition products of (*E*)-5-hydroxy-5-(substituted-phenyl)pent-3-en-2-ones **3**; whereas PPh$_3$ not attacks the C—C double bond of but-3-en-2-one **1** but the C—O double bond of aldehydes **2** and gave the 1,4-addition products of 1-(substituted-phenyl)pentane-1,4-diones. As shown in Scheme 2, in the case of



SCHEME 2

the tris(4-methoxylphenyl)phosphine-catalyzed reaction (part A), tris(4-methoxylphenyl)phosphine reacts with but-3-en-2-one **1** to generate a zwitterionic intermediate **5**, which is in equilibrium with tautomers **7** and **8**. The tautomer **8** serves as a polar reactive species for subsequent 1,2-addition with aldehydes **2**. Then the facile 1,4-proton transfer and elimination take place to give product **3** and regenerate catalyst of tris(4-methoxylphenyl)phosphine. In contrast, the triphenylphosphine-catalyzed pathway (part B) benefits from the proton transfer of **10** to produce α-oxo-ylide **11**. The subsequent Michael (1,4-addition) addition reaction, followed by proton transfer and elimination, produce the target compound **4** and regenerate the catalyst triphenylphosphine.

In conclusion, the presented procedure provides a highly selective synthetic approach for the synthesis of 1-phenylpentane-1, 4-diones, and (*E*)-5-hydroxy-5-phenylpent-3-en-2-ones. Besides, operational simplicity, achievement of selective additions by the choice of different catalysts, and atom-economy are also the merits of this protocol.

EXPERIMENTAL

General Methods

All the reactions were carried out at 60°C in a round bottom flask equipped with a magnetic stir bar. Solvents and all reagents were used as received. 1 H NMR spectra were recorded in $CDCl_3$ at 400 MHz, and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz at South China Agricultural University. The chemical shifts (δ) were referenced to TMS. GC–MS was obtained using electron ionization (EI). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared silica gel plates (GF254), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich (Beijing, China).

Typical Procedure for the Reaction of But-3-en-2-one with 4-Nitrobenzaldehyde (Table 3, entry 1). To a stirring mixture of but-3-en-2-one (70 mg, 1.0 mmol) and 4-nitrobenzaldehyde (151 mg, 1 mmol), 4 mL tetrahydrofuran (THF) and tris(4-methoxylphenyl)-phosphine ($P(p\text{-}PhOCH_3)_3$) (70.4 mg, 0.2 mmol) were added successively. The mixture was stirred under at 60°C for 24 h in a round bottom flask After cooling, the resulting mixture was then analyzed by GC and GC-MS. The solvent was subjected to isolation by PTLC (GF_{254}), eluted with a 10:1 petroleum ether–diethyl ether mixture to afford the desired product and (*E*)-ethyl 4-hydroxy-4-(4-nitrophenyl)but-2-enoate.

Characterization Data for Products

(E)-5-Hydroxy-5-(4-nitrophenyl)pent-3-en-2-one (Table 3, entry 1). Pale yellow viscous oil, IR ν_{max} (KBr): 3421, 1682, 1522, 1459, 1347, 1106, 970, 685, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, 2H), 7.54 (d, 2H), 6.24 (s, 1H), 6.00 (s, 1H), 5.65 (s, 1H), 3.38 (b, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.1, 148.9, 140.8, 133.2, 127.4, 123.6, 123.4, 72.3, 26.4; GC-MS *m/z*: 221.8; Anal. Calcd for

$C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; Found: C, 59.88; H, 5.25.

(E)-5-Hydroxy-5-(3-nitrophenyl)pent-3-en-2-one (Table 3, entry 2). Pale yellow viscous oil, IR ν_{max} (KBr): 3445, 1651, 1575, 1485, 1375, 1195, 1025, 970, 785, 685, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 1H), 8.10 (d, 1H), 7.64 (t, 1H), 7.48 (d, 1H), 6.10 (s, 1H), 5.90 (s, 1H), 5.70 (s, 2H), 3.19 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 148.0, 143.8, 142.0, 131.6, 129.1, 127.5, 122.6, 121.0, 72.1, 26.5; GC-MS *m/z*: 221.35; Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; Found: C, 59.50; H, 5.48.

(E)-5-Hydroxy-5-(4-fluorophenyl)pent-3-en-2-one (Table 3, entry 3). Pale yellow viscous oil, IR ν_{max} (KBr): 3425, 1707, 1509, 1422, 1311, 1150, 1050, 930, 795, 700, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, 2H), 7.00 (d, 2H), 6.18 (s, 1H), 5.95 (s, 1H), 5.59 (s, 1H), 3.96 (b, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 148.2, 139.6, 131.7, 127.5, 127.1, 120.8, 72.3, 19.8; GC-MS *m/z*: 194.31; Anal. Calcd for $C_{11}H_{11}FO_2$: C, 68.03; H, 5.71; Found: C, 67.91; H, 5.55.

(E)-5-Hydroxy-5-(4-chlorophenyl)pent-3-en-2-one (Table 3, entry 4). Colorless viscous oil, IR ν_{max} (KBr): 3422, 1673, 1489, 1367, 1090, 955, 829, 724, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27 (s, 4H), 6.18 (s, 1H), 5.95 (s, 1H), 5.55 (s, 1H), 2.84 (b, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 149.6, 140.0, 133.4, 128.5, 127.9, 127.0, 72.2, 26.4; GC- MS *m/z*: 210.78; Anal. Calcd for $C_{11}H_{11}ClO_2$: C, 62.72; H, 5.26; Found: C, 62.55; H, 5.42.

(E)-5-Hydroxy-5-(4-bromophenyl)pent-3-en-2-one (Table 3, entry 5). Colorless viscous oil, IR ν_{max} (KBr): 3425, 1670, 1487, 1367, 1073, 954, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, 2H), 7.20 (d, 2H), 6.18 (s, 1H), 5.95 (s, 1H), 5.54 (s, 1H), 2.70 (b, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 149.5, 140.5, 131.5, 128.2, 127.0, 121.6, 72.3, 18.0; GC-MS *m/z*: 254.91; Anal. Calcd for $C_{11}H_{11}BrO_2$: C, 51.79; H, 4.35; Found: C, 51.66; H, 4.50.

(E)-5-Hydroxy-5-(4-iodophenyl)pent-3-en-2-one (Table 3, entry 6). Pale yellow viscous oil, IR ν_{max} (KBr): 3418, 1676, 1362, 1162, 1123, 945, 760, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, 2H), 7.04 (d, 2H), 6.04 (s, 1H), 5.94 (s, 1H), 5.84 (s, 1H), 2.58 (b, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 149.6, 140.8, 131.0, 128.8, 127.1, 121.3, 72.3, 19.2; GC-MS *m/z*: 302.5; Anal. Calcd for $C_{11}H_{11}IO_2$: C, 43.73; H, 3.67; Found: C, 43.77; H, 3.90.

1-(4-Nitrophenyl)-1,4-dione (Table 4, entry 1). Pale yellow viscous oil, IR ν_{max} (KBr): 1712, 1687, 1601, 1520, 1345, 1163, 1108, 994, 855, 740, 688, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, 2H), 8.10 (d, 2H), 3.26 (t, 2H), 2.92 (t, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.8, 197.1, 141.1, 129.1, 127.3, 123.9, 37.0, 32.8, 30.0; GC-MS *m/z*: 221.18; Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; Found: C, 59.99; H, 5.23.

1-(3-Nitrophenyl)-1,4-dione (Table 4, entry 2). Pale yellow viscous oil, IR ν_{max} (KBr): 1715, 1651, 1529, 1351, 1230, 1092, 938, 732, 673, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.79 (s, 1H), 8.41 (d, 1H), 8.29 (d, 1H), 7.66 (t, 1H), 3.44 (t, 2H), 2.93 (t, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.7, 196.4, 148.2, 137.9, 133.6, 129.9, 127.4, 123.0, 37.0, 32.5, 30.0; GC-MS *m/z*: 221.50; Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; Found: C, 59.65; H, 5.11.

1-(4-Fluorophenyl)-1,4-dione (Table 4, entry 3). Pale yellow viscous oil, IR ν_{max} (KBr): 1715, 1683, 1599, 1507, 1410, 1360, 1158, 1098, 996, 841, 734, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, 2H), 7.11 (d, 2H), 3.22 (t, 2H), 2.85 (t, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.3, 196.9, 133.1, 130.6, 126.3, 115.9, 37.0. 30.1. 29.7; GC-MS *m/z*: 194.62; Anal. Calcd for $C_{11}H_{11}FO_2$: C, 68.03; H, 5.71; Found: C, 68.20; H, 5.75.

1-(4-Chlorophenyl)-1,4-dione (Table 4, entry 4). Pale yellow viscous oil, IR ν_{max} (KBr): 1710, 1673, 1591, 1489, 1404, 1211, 1162, 1093, 995, 894, 733, 648, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, 2H), 7.42 (d, 2H), 3.21 (t, 2H), 2.87 (t, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.2, 197.3, 139.6, 134.9, 129.5, 128.9, 37.0, 32.3, 30.1; GC-MS *m/z*: 210.55; Anal. Calcd for $C_{11}H_{11}ClO_2$: C, 62.72; H, 5.26; Found: C, 62.85; H, 5.28.

1-(4-Bromophenyl)-1,4-dione (Table 4, entry 5). Pale yellow viscous oil, IR ν_{max} (KBr): 1715, 1671, 1585, 1473, 1378, 1262, 1153, 1025, 991, 899, 740, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, 2H), 7.58 (d, 2H), 3.20 (t, 2H), 2.85 (t, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.2, 197.5, 135.3, 131.9, 129.6, 128.3, 37.0, 32.3, 30.1; GC-MS *m/z*: 255.55; Anal. Calcd for $C_{11}H_{11}BrO_2$: C, 51.79; H, 4.35; Found: C, 51.81; H, 4.35.

1-(4-Iodophenyl)-1,4-dione (Table 4, entry 6). White viscous oil, IR ν_{max} (KBr): 1712, 1665, 1550, 1490, 1370, 1200, 1075, 999, 890, 800, 690, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, 2H), 7.67 (d, 2H), 3.19 (t, 2H), 2.86 (t, 2H), 2.23 (s, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 207.2, 197.4, 134.3, 130.9, 129.1, 1286, 37.1, 31.3, 29.9; GC-MS *m/z*: 302.20; Anal. Calcd for $C_{11}H_{11}IO_2$: C, 43.73; H, 3.67; Found: C, 43.75; H, 3.66.

1-m-Tolypentane-1,4-dione (Table 4, entry 7). Orange viscous oil, IR ν_{max} (KBr): 1715, 1683, 1401, 1357, 1259, 1157, 1087, 794, 760, 690, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, 2H), 7.34 (m, 2H), 3.24 (t, 2H), 2.84 (t, 2H), 2.38 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.4, 198.7, 138.3, 136.6, 133.9, 128.6, 128.4, 125.2, 37.1, 32.5, 30.1, 21.3; GC-MS *m/z*: 190.88; Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.56; H, 7.42; Found: C, 75.37; H, 7.38.

1-Penylpentane-1,4-dione (Table 4, entry 8). Orange viscous oil, IR ν_{max} (KBr): 1717, 1683, 1450, 1359, 1159, 1082, 996, 743, 691, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, 2H), 7.53 (t, 1H), 7.44 (t, 2H), 3.28 (t, 2H), 2.87 (t, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.4, 198.5, 135.9, 133.2, 128.6, 128.0, 37.1, 32.4, 30.1; GC-MS *m/z*: 176.33; Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86; Found: C, 75.20; H, 6.90.

1-(Furan-2-yl)pentane-1,4-dione (Table 4, entry 9). Orange viscous oil, IR ν_{max} (KBr): 1713, 1670, 1569, 1489, 1398, 1190, 1065, 789, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, 1H), 7.18 (d, 1H), 6.51 (q, 1H), 3.11 (t, 2H), 2.84 (t, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.1, 187.7, 152.4, 146.3, 117.1, 112.2, 36.7, 32.0, 30.0; GC-MS *m/z*: 166.20; Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07; Found: C, 64.90; H, 6.30.

REFERENCES

[1] (a) Mennen, S. M.; Blank, J. T.; Tran-Dubé, M. B.; Imbriglio, J. E.; Miller, S. J. Chem Commun 2005, 195–197; (b) Enders, D.; Han, J. W.; Henseler, A. Chem Commun 2008, 3989–3991; (c) Enders, D.; Niemeier, O.; Henseler A. Chem Rev 2007, 107, 5606–5655; (d) List, B. J. Acc Chem Res 2004, 37, 548–557; (e) Otte, R. D.; Sakata, T.; Guzei, I. A.; Lee, D. Org Lett 2005, 7, 495–498; (f) Nair, V.; Biju, A. T.; Abhilash, K. G.; Menon, R. S.; Suresh, E. Org Lett 2005, 7, 2121–2123; (g) Nair, V.; Biju, A. T.; Vinod, A. U. Org Lett 2005, 7, 5139–5142.

[2] (a) O'Donovan, B. F.; Hitchcock, P. B.; Meidine, M. F.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. Chem Commun 1997, 81–82; (b) Zhu, G.; Chen, Z.; Jiang, Q.; Xiao, D.; Cao, P.; Zhang, X. J Am Chem Soc 1997, 119, 3836–3837; (c) Kumar, K.; Kapur, A.; Ishar, M. P. S. Org Lett 2000, 2, 787–789; (d) Ramazani, A.; Bodaghi, A. Tetrahedron Lett 2000, 41, 67–568.

[3] For reviews on phosphine-mediated reactions, see: (a) Methot, J. L.; Roush, W. R. Adv Synth Catal 2004, 346, 1035–1050; (b) Lu, X.; Zhang, C.; Xu, Z. Acc Chem Res 2001, 34, 535–544.

[4] (a) Drewes, S. E.; Roos, G. H. P. Tetrahedron 1988, 44, 4653–4655; (b) Basavaiah, D.; Rao, P. D.; Hyma, R. S. Tetrahedron 1996, 52, 8001–8004; (c) In Organic Reactions; Paquette, L. A. (Ed.); Wiley: New York, 1997; Vol. 51, pp. 201–350; (d) Basavaiah, D.; Kumaragurubaran, N.; Sharada, D. S. Tetrahedron Lett 2001, 42, 85–87; (e) Yang, K. S.; Chen, K. Org Lett 2000, 2, 729–732; (f) Chamakh, A.; Amri, H. Tetrahedron Lett 1998, 39, 375–377; (g) Basavaiah, D.; Kumaragurubaran, N. Tetrahedron Lett 2001, 42, 477–480; (h) Rafel, S.; Leahy, J. W. J Org Chem 1997, 62, 1521–1522; (i) Hayase, T.; Shibata, T.; Soai, K.; Wakatsuki, Y. Chem Commun 1998, 1271–1272.

[5] (a) Kundu, M. K.; Mukherjee, S. B.; Balu, N.; Padmakumar, R.; Bhat, S. V. Synlett 1994, 444–446; (b) Hill, J. S.; Isaacs, N. S. Tetrahedron Lett 1986, 27, 5007–5009; (c) Kamimura, A.; Omata, Y.; Mitsudera, H.; Kakehi, A. J. Chem Soc, Perkin Trans 1 2000, 4499–4501; (d) Youn, S. W.; Park, H. S.; Kim, Y. H. Chem Commun 2000, 2005–2006.

[6] (a) Jefford, C. W.; Kohmoto, S.; Jaggi, D.; Timari, G. Hel Chim Acta 1995, 78, 647–62; (b) Kazuhiro, T.; Tetsuji, O.; Nobuyoshi, H.; Chiaki, K.; Atsushi, K.; Hideo, K. Eur Pat Appl 1995, 132–135; (c) Huang, D.; Yan, M.; Zhao, W. J.; Shen, Q. Synth Commun 2005, 35, 745–750; (d) Stetter, H. Angew Chem, Int Ed 1976, 15, 639–641; (e) Enders, D.; Breuer, K.; Runsink, J. Helv Chim Acta 1996, 79, 1899–1902; (f) Stetter, H.; Hilboll, G.; Kuhlmann, H. Chem Ber 1979, 112, 84–86; (g) Stetter, H.; Basse, W.; Nienhaus, J. Chem Ber 1980, 113, 690–692; (h) Stetter, H.; Mohrmann, K.-H.; Schlenker, W. Chem Ber 1981, 114, 581–583; (i) Stetter, H.; Bender, H. J. Chem Ber 1981, 114, 1226–1229; (j) Stetter, H.; Haese, W. Chem Ber 1984, 117, 682–684.

[7] (a) Han, X. J. Tetrahedron Lett 2007, 48, 2845–2849; (b) Santiago, R.; Maria, K.; Javier, I.; Irakusne, L.; Gabriel, P. Tetrahedron 2006, 62, 11112–11123; (c) Srinivasa, R. K.; Mukkanti, K.; Srinivasa, R. D. Tetrahedron Lett 2005, 46, 2287–2290; (d) Jan, M.; Mathieu, P.; Johannes, B. Tetrahedron 2000, 56, 2491–2495.

[8] (a) Gong, J. H.; Im, Y. I.; Lee, K. Y.; Kim, J. N. Tetrahedron Lett 2002, 43, 1247–1251; (b) Maeda, H.; Maki, T.; Ashie, H.; Ohmori, H. J Chem Soc, Chem Commun 1995, 871–873; (c) Ciganek, E. Synthesis 1995, 1311–1312; (d) Stetter, H.; Kuhlmann, H. In Organic Reactions; Paquette, L. A. (Ed.); Wiley: New York, 1991, Vol. 40, 407–496; (e) Kim, J. N.; Lee, K. Y.; Kim, H. S.; Kim, T. Y. Org Lett 2000, 2, 343–245; (f) Kim, H. S.; Kim, T. Y.; Lee, K. Y.; Chung, Y. M.; Lee, H. J.; Kim, J. N. Tetrahedron Lett 2000, 41, 2613–2165; (g) Kim, J. N.; Im, Y. J.; Gong, J. H.; Lee, K. Y. Tetrahedron Lett 2001, 42, 4195–4197; (h) Lee, H. J.; Kim, H. S.; Kim, J. N. Tetrahedron Lett 1999, 40, 4363–4365; (i) Lee, H. J.; Seong, M. R.; Kim, J. N. Tetrahedron Lett 1998, 39, 6223–6225; (j) Yamada, Y. M. A.; Ikegami, S. Tetrahedron Lett 2000, 41, 2165–2167.