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Samarium reagent-promoted formation of benzoins from diarylmethanones and DMF via a carbene rearrangement reaction

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Abstract—Prompted by samarium metal in DMF with TMSCl or iodine as an activator, or by SmI_2/THF system, diarylmethanones react readily with DMF to afford benzoins in moderate to good yields via rearrangement of aryl groups. As for asymmetric diarylmethanones, products resulting from the migration of either aryl group were obtained, where the migration of aryl groups shows certain priority.

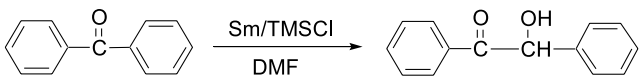
1. Introduction

Since the pioneering studies of Kagan and his co-workers demonstrated the particular effectiveness of samarium diiodide (SmI_2) as a powerful one-electron transfer reductant, the utilization of SmI_2 in synthetic organic synthesis has been widely documented.[1] Although samarium diiodide is a very useful reducing reagent, its application in organic synthesis is, to some extent, limited. Its storage is difficult due to its sensitivity to air oxidation. Besides, Sm^{2+} can only donate one electron in the reaction and the lack of atom economy seriously restricts its large scale application. Therefore, the direct use of metallic samarium as a reducing agent in organic transformations has attracted the attention of many organic chemists.[2] Usually, reactions promoted directly by samarium metal are carried out in THF,[3] and metallic samarium has to be activated by other reagents such as iodine, hydrochloric acid, alkyl halides, TMSCl, etc.[1,3,4] so as to ensure that the reactions proceed smoothly. We recently found that metallic samarium exhibits some interesting properties in organic synthesis when *N*,*N*-dimethylformamide (DMF) is used as a solvent instead of THF.[5]

The diarylmethanone dianion is a known species[6] whose reactions with carbonyl compounds or benzonitrile have long been observed.[7] Reduced by SmI_2, diarylmethanone readily forms ketyl, which has considerable stability and constitutes the important intermediate in cross-coupling reactions with ketones, aldehydes, imines, aroyl chlorides, conjugated carbon–carbon double bonds, and so on.[1]

2. Results and discussion

However, when diphenylmethanone was treated with samarium metal activated by TMSCl in DMF, surprisingly, benzoin was obtained in excellent yield (Scheme 1).



Scheme 1.

The unexpected formation of benzoin indicates that the additional carbonyl group comes from dimethylformamide, and the dimethylamino group acts as a leaving group in this reaction. Despite the fact that the carbonyl groups of amides are unreactive towards many carbon nucleophiles and are consequently employed as solvents in carbon–carbon bond-formation reactions,[8] DMF is well known for being a good formylation reagent (Vilsmeier–Haack reaction).[9] Besides, such necleophiles as Grignard reagents,[10a] organolithium[10a,b] and the radical anions[10c] resulting from the reduction by sodium in THF can attack the carbonyl group in DMF to afford the corresponding aldehydes. In the reactions mentioned above, the formoyl group in DMF was

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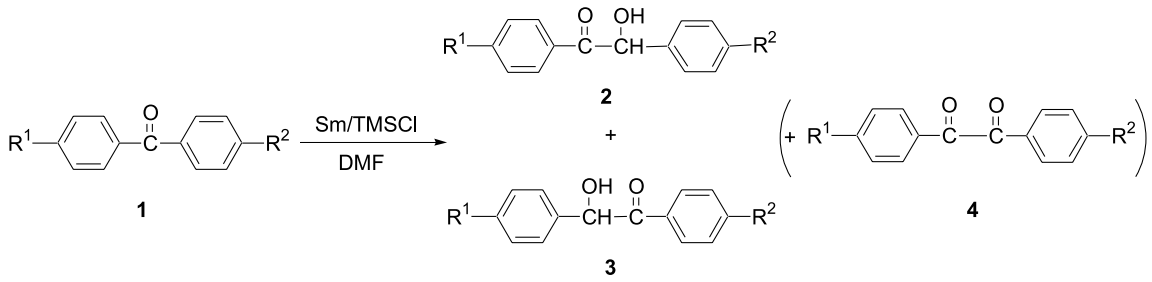


Scheme 2.

introduced into the products, with dimethylamino anion acting as a leaving group.

To have some idea about the mechanism of such a reaction, we carried out an extensive literature survey and were fortunate to find some clues to this reaction in the electron spin resonance study of the radicals obtained from acetophenone and benzaldehyde.[11] At high reduction potentials and by an irreversible electrode process, the conversion of acetophenone to 1-phenyl-propane-1,2-semidione in DMF was proposed to undergo a carbene rearrangement.[11b]

2.1. Sm/TMSCl-promoted formation of benzoin from diarylmethanone in DMF

To have an in-depth understanding of the reaction, a series of diarylketones were subjected to the same conditions and the desired benzoins were formed smoothly. In some cases, benzils were also obtained as unexpected byproducts (Scheme 2).

The results of the reactions are shown in Table 1.

The reaction of diarylketones with electron-donating group attached to the aromatic rings proceeded efficiently. In contrast, diarylketones with electron-withdrawing group require a relatively harsh reaction conditions and gave lower total yields. As can be seen, bis(*p*-methylphenyl)-methanone (**1b**) and bis(*p*-methoxyphenyl)-methanone (**1c**) produced 4,4′-dimethylbenzoin and anisoin, respectively (entries 2 and 3) in good yields, while bis(*p*-chlorophenyl)-methanone (**1e**) failed to afford the corresponding types of products **2** and **3**. It was surprising to find that bis(*p*-dimethylaminophenyl)-methanone (**1d**) did not undergo the reaction under the same conditions. The amino group might have some effects on TMSCl and thus bear an electron-withdrawing character, which made it difficult for the reaction to occur, as in the case of bis(*p*-chlorophenyl)-methanone (**1e**). As for asymmetric diarylmethanones, two kinds of benzoins could be obtained, with the carbonyl groups adjacent to the electron-richer aryl groups being predominant. This may indicate that the reaction followed a certain rule in the rearrangement.

It is worth noting that besides the 4′-chlorobenzoin (**3h**), benzoin (**2a**) was also obtained (entry 8). The formation of **2a** obviously resulted from a dechlorination process under the reaction conditions accompanying the rearrangement. As for phenyl *p*-bromophenyl methanone, the debromination reaction proceeded to such an extent that benzoin (**2a**) was isolated as the only product. Attempt was also made to investigate whether acetophenone and benzaldehyde could undergo such a reaction, but the result was negative.

2.2. Sm/I_2-promoted formation of benzoin from diarylmethanone in DMF

Considering that TMSCl is an acidic activator, we explored neutral activator iodine in our further investigations. To our delight, better results were obtained in the presence of I_2, as shown in Table 2.

With iodine as an activator, the reaction proceeded more easily in milder reaction conditions and produced higher total yields than that activated by TMSCl, except that substrate bis-(*p*-chlorophenyl)-methanone (**1e**) still failed to

Table 1. Reactions of diarylmethanones with DMF promoted by Sm/TMSCl in DMF

Entry	R^1, R^2 in substrate **1**	Temperature (°C)	Time (h)	Total yield of **2**, **3** (%)[a]	Ratio[b] of **2**/**3**	Yield of **4** (%)
1	H, H (**1a**)	90	10	91 (**2a**)		0 (**4a**)
2	4-CH_3, 4-CH_3 (**1b**)	80	6	74 (**2b**)		18 (**4b**)
3	4-CH_3O, 4-CH_3O (**1c**)	80	4	53 (**2c**)		35 (**4c**)
4	4-$(CH_3)_2N$, 4-$(CH_3)_2N$ (**1d**)	120	36	—		—
5	4-Cl, 4-Cl (**1e**)	120	12	—		—
6	4-CH_3, H (**1f**)	90	8	77 (**2f**, **3f**)	68/32	14 (**4f**)
7	4-Ph, H (**1g**)	80	5	47[c] (**2g**, **3g**)	19/81	16 (**4g**)
8	4-Cl, H (**1h**)	120	24	52[d] (**2a**, **3h**)	0/100	0
9	4-Br, H (**1i**)	120	24	53[e] (**2a**)		0

[a] Products **2** and **3** were inseparable and the overall yields were given.
[b] The ratio was determined by HPLC and ^{1}H NMR.
[c] A considerable amount of reductive product biphenyl-4-yl-phenyl-methanol was detected.
[d] Dechlorination reaction affording 26% of **2a** occurred simultaneously in the formation of the corresponding benzoin.
[e] Exclusive debromination product **2a** was formed.

Table 2. Reaction of diarylmethanones with DMF promoted by Sm/I_2 in DMF

Entry	R^1, R^2 in substrate **1**	Temperature (°C)	Time (h)	Total yield of **2**, **3** (%)	Ratio of **2/3**	Yield of **4** (%)
1	H, H (**1a**)	80	2	90 (**2a**)[12b]		0
2	4-CH_3, 4-CH_3 (**1b**)	70	1	79 (**2b**)[12b]		15 (**4b**)[12f]
3	4-CH_3O, 4-CH_3O (**1c**)	50	1	78 (**2c**)[12b]		16 (**4c**)[12f]
4	4-$(CH_3)_2N$, 4-$(CH_3)_2N$ (**1d**)	80	1	63 (**2d**)[12d]		21 (**4d**)[12f]
5	4-Cl, 4-Cl (**1e**)	120	5	—		—
6	4-CH_3, H (**1f**)	70	1	82 (**2f**, **3f**)[12c]	68/32	11 (**4f**)[12g]
7	4-Ph, H (**1g**)	50	1	87 (**2g**, **3g**)[12e]	81/19	9 (**4g**)[12h]
8	4-Cl, H (**1h**)	100	5	41 (**2h**, **3h**)[12c]	0/100	13 (**4h**)[12f]
9	4-Br, H (**1i**)	100	5	58 (**2a**)		0

give encouraging results (entry 5). Bis-(*p*-dimethylaminophenyl)-methanone, to our expectations, underwent the same kind of reactions under similar conditions and afforded the corresponding benzoin and benzil in high total yield (entry 4). The benzoins with the carbonyl groups adjacent to the electron-richer aryl groups still predominated in the products when asymmetric diarylmethanones were used as substrates under the $Sm/DMF/I_2$ conditions. An exception was that biphenyl-4-yl-phenyl-methanone (**1g**) produced the benzoin with the carbonyl group adjacent to the biphenyl group as the major product (entry 7). However, the relationship between the reaction chemoselectivity and activator remains unclear.

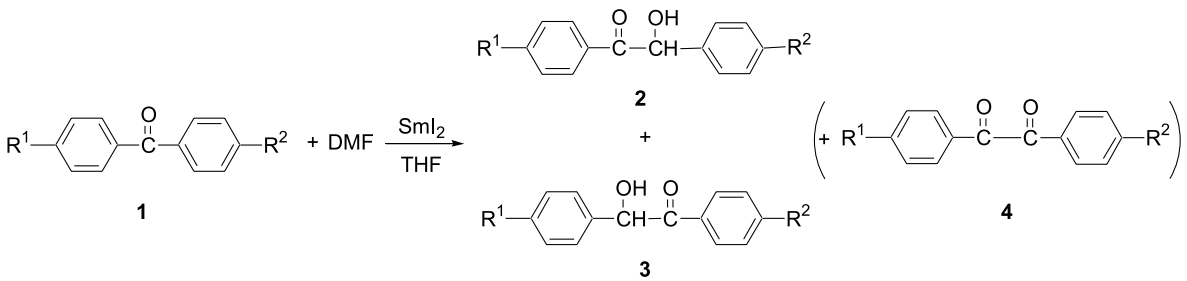
2.3. SmI_2-promoted formation of benzoin from diarylmethanone and DMF in THF

We made the attempt and found that without activator (TMSCl or I_2) the reaction could not occur at all, and further attempts to expand the reaction to other metal such as zinc failed. We also tried other solvents instead of DMF, such as THF, DMSO and toluene, but did not detect any formation of benzoin. This result may indicate that the additional carbonyl group came from DMF.

Therefore, we made further investigations to find out whether or not SmI_2 can promote the coupling rearrangement reaction of diarylmethanone and DMF in THF. To our expectations, the reaction occurred smoothly and completed in a very short time, despite a relatively low total yield and more byproduct benzil (Scheme 3, Table 3). The chemoselectivity of rearrangement reaction is generally similar to that in the $Sm/DMF/I_2$ system.

2.4. Possible mechanism

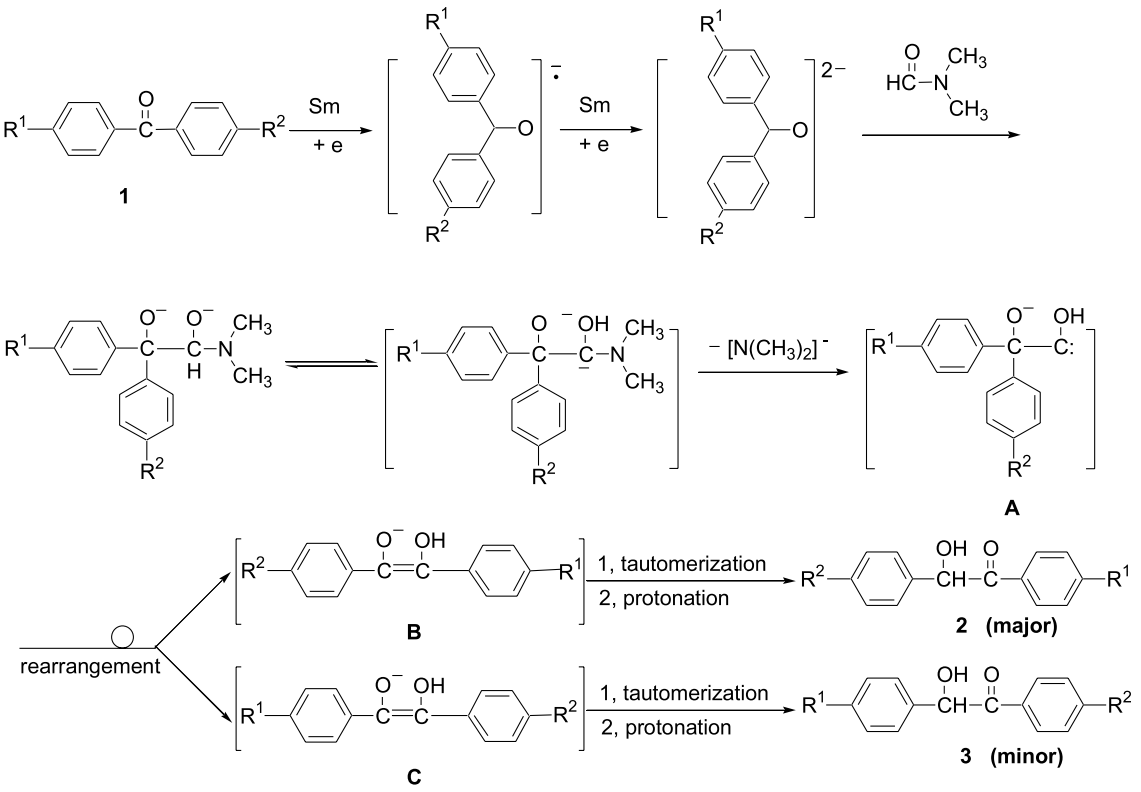
The formation of benzils could be explained as a result of the auto-oxidation of benzoins. The presence of reports claiming that some metal salts such as copper (I)[13a] and Ce (IV)[13b] could easily catalyze the autoxidation of benzoins into the corresponding benzils made us deduce that the presence of samarium salts might have accelerated the formation of benzils from benzoins during the treatment process. Further investigations showed that the benzil



Scheme 3.

Table 3. Reaction of diaryl-methanones with DMF promoted by SmI_2 in THF

Entry	R^1, R^2 in substrate **1**	Total yield of **2**, **3** (%)	Ratio of **2/3**	Yield of **4** (%)
1	H, H (**1a**)	42 (**2a**)		39 (**4a**)[12f]
2	4-CH_3, 4-CH_3 (**1b**)	29 (**2b**)		51 (**4b**)
3	4-CH_3O, 4-CH_3O (**1c**)	48 (**2c**)		36 (**4c**)
4	4-$(CH_3)_2N$, 4-$(CH_3)_2N$ (**1d**)	33 (**2d**)		31 (**4d**)
5	4-Cl, 4-Cl (**1e**)	0		0
6	4-CH_3, H (**1f**)	42 (**2f**, **3f**)	71/29	31 (**4f**)
7	4-Ph, H (**1g**)	27 (**2g**, **3g**)	78/22	39 (**4g**)
8	4-Cl, H (**1h**)	0		0
9	4-Br, H (**1i**)	0		0



Scheme 4.

could also have been obtained when benzoin was treated under the same reaction conditions. This validates our suggestion.

We made the attempt and found that without activator (TMSCl or I_2) the reaction could not occur at all, and further attempts to expand the reaction to other metal such as zinc failed. On the other hand, the fact that without diarylmethanone in the reaction system, no obvious reaction between Sm/activator and DMF was observed shows the reaction must be initiated by ketyl resulting from diarylmethanone. Based on our experimental results and the ESR studies on the relevant radicals,[11b] a possible mechanism is suggested (Scheme 4).

Due to the strongly electrophilic character of carbene,[14] **A** undergoes a rearrangement (intramolecular insertion reaction) in which the electron-richer aryl group of the two preferably migrates to form enol intermediates (**B**>**C**), which in turn tautomerize immediately, and are followed by protonation to give the corresponding benzoins, respectively.

In conclusion, with TMSCl or iodine as the activator in DMF or performed in SmI_2/THF system, the reaction between diarylketones and DMF via a rearrangement process promoted by samarium metal can afford benzoins and benzils in good overall yields. The complexing of DMF with samarium ion[15] may have played an important role in enabling the reaction to occur, and studies on the exact mechanism are currently in progress.

3. Experimental

3.1. General

All ^{1}H NMR spectra were measured in $CDCl_3$ and recorded on Brucker Avance-400 (400 MHz) spectrometer with TMS as the internal standard. Chemical shifts are expressed in ppm and *J* values are given in Hz. IR spectra were run on a Bruck vector 22 spectrometer. EI-MS were determined with a HP5989B mass spectrometer. Melting points are uncorrected. All the reactions in this paper were performed under nitrogen atmosphere. DMF was redistilled and dried over molecular sieve before use.

3.2. Sm/DMF/TMSCl system promoted rearrangement reaction of diarylketones with DMF

General procedure. To a mixture of Sm powder (2 mmol) and diarylketone (2 mmol) in freshly distilled *N*,*N*-dimethylformamide (DMF, 10 mL) TMSCl (0.2 mL, freshly distilled) was added at room temperature, with magnetic stirring under a nitrogen atmosphere. The reaction mixture was then heated to a certain temperature so as to ensure that the reaction occurred (as indicated in Table 1). After the completion of the reaction (monitored by TLC), dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture was extracted with diethyl ether (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude products were purified with flash chromatography (silica/hexanes–ethyl

acetate, 9:1 v/v) to afford the corresponding benzoins and/or benzils.

3.3. Sm/DMF/I_2 system promoted rearrangement reaction of diarylketones with DMF

General procedure. To a mixture of Sm powder (2 mmol) and diarylketone (2 mmol) in freshly distilled *N*,*N*-dimethylformamide (DMF, 10 mL) I_2 (0.13 g, 0.5 mmol) was added at room temperature, with magnetic stirring under a nitrogen atmosphere. The reaction mixture was then heated to a certain temperature so as to ensure that the reaction occurred (as indicated in Table 2). After the completion of the reaction (monitored by TLC), dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture was extracted with diethyl ether (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude products were purified with flash chromatography (silica/hexanes–ethyl acetate, 9:1 v/v) to afford the corresponding benzoins and/or benzils.

3.4. SmI_2/THF system promoted rearrangement reaction of diarylketones with DMF

General procedure. To a solution of SmI_2 (3 mmol) in THF (20 mL), diarylketone (1 mmol) was added at room temperature under a nitrogen atmosphere. The deep blue color of the solution turned red immediately, and DMF (0.5 mL) was added. The color of resultant solution vanished immediately, which indicated that the reaction had completed. After being stirred for 5–10 min, dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture was extracted with diethyl ether (3×20 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude products were purified with flash chromatography (silica/hexanes–ethyl acetate, 9:1 v/v) to afford the corresponding benzoins and/or benzils.

3.4.1. 2-Hydroxy-1,2-diphenyl-ethanone (2a). White solid, mp 134–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.95 (m, 2H), 7.52–7.54 (m, 1H), 7.40–7.44 (m, 2H), 7.28–7.36 (m, 5H), 5.97 (d, 1H, J=6.0 Hz), 4.56 (d, 1H, J=6.0 Hz); IR (KBr) 3417, 3060, 2933, 1680, 1596, 1491, 1450 cm^{-1}; mass spectrum, *m*/*z* (relative intensity, %) 213 (1.16, M^++1), 212 (0.43, M^+), 195 (13.95, M^+−OH), 107 (61.01), 105 (100), 77 (89.62). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.48; H, 5.74.

3.4.2. 2-Hydroxy-1,2-di-*p*-tolyl-ethanone (2b). White solid, mp 86–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.85 (m, 2H), 7.19–7.24 (m, 4H), 7.13–7.15 (m, 2H), 5.91 (d, 1H, J=6.0 Hz), 4.55 (d, 2H, J=6.0 Hz), 2.37 (s, 3H), 2.31 (s, 3H); ^{13}C NMR δ ($CDCl_3$): 198.6, 144.9, 138.3, 136.4, 131.0, 129.8, 129.4, 129.3, 127.7, 75.8, 21.7, 21.2; IR (KBr) 3473, 3038, 2921, 1676, 1607, 1513 cm^{-1}; mass spectrum, *m*/*z* (relative intensity, %) 241 (0.36, M^++1), 240 (1.20, M^+), 223 (1.79, M^+−OH), 121 (85.90), 119 (95.45, M^+), 91 (100). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.68; H, 6.73.

3.4.3. 2-Hydroxy-1,2-bis-(4-methoxyphenyl)-ethanone (2c). White solid; mp 111–113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.94 (m, 2H), 7.25–7.28 (m, 2H), 6.85–6.90 (m, 4H), 5.87 (d, 1H, J=5.2 Hz), 4.60 (d, 1H, J=5.2 Hz), 3.84 (s, 3H), 3.78 (s, 3H); ^{13}C NMR δ ($CDCl_3$): 197.3, 164.0, 159.6, 132.4, 131.9, 131.6, 129.0, 114.5, 113.9, 75.3, 55.5, 55.2; IR (KBr) 3465, 3077, 2939, 1667, 1598, 1514, 1469 cm^{-1}; mass spectrum, *m*/*z* (relative intensity, %) 272 (0.61, M^+), 255 (0.88, M^+−OH), 137 (100), 135 (86.2), 107 (17.31), 77 (80.38). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.89; H, 5.88.

3.4.4. 1,2-Bis-(4-dimethylamino-phenyl)-2-hydroxy-ethanone (2d). White solid; mp 153–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.88 (m, 2H), 7.20–7.22 (m, 2H), 6.66–6.68 (m, 4H), 5.80 (d, 1H, J=6.0 Hz), 4.68 (d, 1H, J=6.0 Hz), 2.92 (s, 6H), 3.03 (s, 6H); ^{13}C NMR δ ($CDCl_3$): 196.6, 154.2, 153.6, 132.2, 131.5, 128.6, 110.8, 110.6, 74.9, 40.1, 39.9; IR (KBr) 3420, 2916, 1681, 1595, 1546, 1483 cm^{-1}; mass spectrum, *m*/*z* (relative intensity, %) 298 (0.24, M^+), 150 (2.16), 148 (100), 120 (5.51). Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.46; H, 7.43; N, 9.39. Found: C, 72.54; H, 7.50; N, 9.45.

3.4.5. 2-Hydroxy-2-phenyl-1-*p*-tolyl-ethanone (2f). The title compound was obtained as a mixture with **3f**; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.85 (m, 2H), 7.14–7.35 (m, 7H), 5.94 (d, 1H, J=6.0 Hz), 4.61 (d, 1H, J=6.0 Hz), 2.38 (s, 3H); IR (KBr) 3441, 3059, 2945, 1675, 1607, 1510, 1491, 1452, 1390 cm^{-1}; mass spectrum, *m*/*z* (relative intensity, %) 227 (0.28, M^++1), 226 (0.72, M^+), 209 (2.59, M^+−OH), 119 (100), 107 (10.37), 91 (55.09), 77 (57.75). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.48; H, 6.28.

3.4.6. 2-Hydroxy-1-phenyl-2-*p*-tolyl-ethanone (3f). The title compound was obtained as a mixture with **2f**; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.95 (m, 2H), 7.15–7.37 (m, 7H), 5.94 (d, 1H, J=6.0 Hz), 4.52 (d, 1H, J=6.0 Hz), 2.31 (s, 3H); IR (KBr) 3441, 3059, 2945, 1675, 1607, 1510, 1491, 1452, 1390 cm^{-1}; mass spectrum, *m*/*z* (relative intensity, %) 227 (0.28, M^++1), 226 (0.72, M^+), 209 (2.59, M^+−OH), 121 (82.30), 105 (24.30), 91 (55.09), 77 (57.75). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.48; H, 6.28.

3.4.7. 1-Biphenyl-4-yl-2-hydroxy-2-phenyl-ethanone (2g). The title compound was obtained as a mixture with **3g**; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–8.03 (m, 2H), 7.29–7.65 (m, 12H), 6.00 (d, 1H, J=6.0 Hz), 4.60 (d, 1H, J=6.0 Hz); IR (KBr) 3422, 3031, 1678, 1603, 1560, 1487, 1450, 1407 cm^{-1}; mass spectrum, *m*/*z* (relative intensity, %) 181 (38.10), 153 (19.85), 107 (6.91), 77 (100). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.10; H, 5.56.

3.4.8. 2-Biphenyl-4-yl-2-hydroxy-1-phenyl-ethanone (3g). The title compound was obtained as a mixture with **2g**; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–8.00 (m, 2H), 7.29–7.65 (m, 12H), 6.02 (d, 1H, J=6.0 Hz), 4.59 (d, 1H, J=6.0 Hz); IR (KBr) 3422, 3031, 1678, 1603, 1560, 1487, 1450, 1407 cm^{-1}; mass spectrum, *m*/*z* (relative intensity, %) 183 (32.29), 153 (19.85), 105 (28.57), 77

(100). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.10; H, 5.56.

3.4.9. 2-(4-Chloro-phenyl)-2-hydroxy-1-phenyl-ethanone (3h). White solid; mp 113–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.92 (m, 2H), 7.54–7.57 (m, 1H), 7.28–7.46 (m, 6H), 5.96 (d, 2H, J=6.0 Hz), 4.56 (d, 1H, J=6.0 Hz); IR (KBr) 3417, 3027, 1679, 1618, 1596, 1450 cm^{-1}; mass spectrum, *m/z* (relative intensity, %) 248 (0.07, M^++2), 246 (0.20, M^+), 229 (0.55, M^+−OH), 141 (13.71), 105 (100), 77 (76.76). Anal. Calcd for $C_{14}H_{11}ClO_2$: C, 68.16; H, 4.50. Found: C, 68.28; H, 4.47.

3.4.10. 1,2-Di-phenyl-ethane-1,2-dione (4a). Yellow crystal (CCl_4); mp 95–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.99 (4H, m), 7.64–7.69 (2H, m), 7.50–7.53 (4H, m); IR (KBr): 3064, 1660, 1594, 1450, 1211, 719, 643 cm^{-1}; mass spectrum, *m/z* (relative intensity, %) 210 (1.77, M^+), 105 (100), 77 (45.51). Anal. Calcd for $C_{14}H_{10}O_2$: C, 79.99; H, 4.79. Found: C, 80.10; H, 4.80.

3.4.11. 1,2-Di-*p*-tolyl-ethane-1,2-dione (4b). Yellow crystal (CCl_4); mp 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.89 (m, 4H), 7.31–7.33 (m, 4H), 2.45 (s, 6H); ^{13}C NMR δ ($CDCl_3$): 194.5, 146.1, 130.7, 130.0, 129.7, 21.9; IR (KBr) 3063, 2919, 1662, 1605, 1573, 1447, 1410 cm^{-1}; mass spectrum, *m/z* (relative intensity, %) 239 (0.37, M^++1), 238 (1.84, M^+), 119 (100), 91 (40.17). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.48; H, 5.90.

3.4.12. 1,2-Bis-(4-methoxyphenyl)-ethane-1,2-dione (4c). Yellow crystal (CCl_4); mp 132–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.98 (m, 4H), 6.98–7.00 (m, 4H), 3.91 (s, 6H); ^{13}C NMR δ ($CDCl_3$): 193.5, 164.9, 132.4, 126.3, 114.3, 55.6; IR (KBr) 3026, 2959, 1656, 1600, 1573, 1510, 1458 cm^{-1}; mass spectrum, *m/z* (relative intensity, %) 271 (0.16, M^++1), 270 (0.87, M^+), 135 (100), 107 (13.77). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.48; H, 5.30.

3.4.13. 1,2-Bis-(4-dimethylamino-phenyl)-ethane-1,2-dione (4d). Yellow crystal (CCl_4); mp 201–204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.89 (m, 4H), 6.57–6.59 (m, 4H), 3.09 (s, 12H); ^{13}C NMR δ ($CDCl_3$): 194.0, 169.1, 121.6, 121.1, 112.8, 40.5; IR (KBr) 2916, 1644, 1595, 1546, 1483 cm^{-1}; mass spectrum, *m/z* (relative intensity, %) 297 (1.41, M^++1), 296 (6.48, M^+), 148 (100), 120 (5.51). Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.62; H, 6.77, 9.41.

3.4.14. 1-Phenyl-2-*p*-tolyl-ethane-1,2-dione (4f). Yellow crystal (CCl_4); mp 30–31 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–8.00 (m, 2H), 7.87–7.90 (m, 2H), 7.64–7.67 (m, 1H), 7.50–7.54 (m, 2H), 7.30–7.34 (m, 2H), 2.45 (s, 3H); IR (KBr) 3062, 2924, 1672, 1605, 1581, 1450 cm^{-1}; mass spectrum, *m/z* (relative intensity, %) 225 (0.23, M^++1), 224 (0.95, M^+), 119 (100), 105 (38.86), 91 (45.30), 77 (31.63). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.38; H, 5.38.

3.4.15. 1-Biphenyl-4-yl-2-phenyl-ethane-1,2-dione (4g). Yellow crystal (CCl_4); mp 103–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–8.09 (m, 4H), 7.75–7.77 (m, 2H), 7.65–7.70 (m, 3H), 7.49–7.57 (m, 5H); ^{13}C NMR δ ($CDCl_3$): 194.6, 194.2, 147.6, 139.5, 134.9, 133.0, 131.7, 130.5, 130.0, 129.1, 128.7, 127.7, 127.4, 127.3; IR (KBr) 3062, 1673, 1594, 1580, 1485, 1449 cm^{-1}; mass spectrum, *m/z* (relative intensity, %) 287 (0.16, M^++1), 286 (0.51, M^+), 181 (100), 153 (22.18), 105 (22.77), 77 (33.18). Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.75; H, 4.97.

3.4.16. 1-(4-Chloro-phenyl)-2-phenyl-ethane-1,2-dione (4h). Yellow crystal (CCl_4); mp 73–74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–8.16 (m, 4H), 7.52–7.60 (m, 5H); IR (KBr) 3023, 1679, 1139, 1609, 1596, 1450 cm^{-1}; mass spectrum, *m/z* (relative intensity, %) 246 (0.18, M^++2), 244 (0.55, M^+), 139 (13.65), 105 (100), 77 (66.67). Anal. Calcd for $C_{14}H_9ClO_2$: C, 68.72; H, 3.71. Found: C, 68.58; H, 3.77.

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