# Synthesis of novel cyclopentenone derivatives and crystal structure determination of 3,4-*bis*(4-chlorophenyl)-5,5- dimethyl-4-hydroxy-2-cyclopenten-1-one

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New cyclopentenone derivatives were prepared via aldol condensation of substituted benzils with acetone derivatives in alkaline media. The structures of products were confirmed by elemental analysis, IR, $^1$H NMR, $^{13}$C NMR and mass spectroscopy and supported by a single crystal X-ray diffraction analysis of 3,4-*bis*(4-chlorophenyl)-5,5- dimethyl-4-hydroxy-2-cyclopenten-1-one. The crystal structure of title compound in the solid state is stabilised by O–H…O and C–H…O hydrogen bonds, as well as by Cl…Cl close contacts.

**Keywords:** Aldol condensation, Cl–Cl close contact, crystal structure, cyclopenteneone, substituted benzils

The cyclopentenone moiety is present in a wide variety of natural products and drug targets.[1] Cyclopentenones are of interest for their anti tumour and anti diabetic,[2,3] pesticide and bactericide[4] properties. They have also been used as commercial labelling materials because of their photochemical properties.[5] Substituted cyclopentenones are used in, cosmetic and related applications.[6] In addition, cyclopentenone moiety is a very useful building block for the synthesis of other biologically active compounds containing five membered rings, due to the reactivity of the α,β-unsaturated carbonyl functionality.

Cyclopetenones have been synthesised by the Pauson–Khand reaction,[7-11] Nazarov cyclisation[12] and Rautenstrauch rearrangement. [13] The aldol condensation of α-diketones with acetone derivatives is an efficient method for preparation of cyclopentenone derivatives. This method is flexible, as there are several simple routes available for preparation of α-diketones.[14-17] Here, we report the synthesis of some new cyclopentenone derivatives via aldol condensation, and also describe a single crystal X-ray diffraction analysis.

## Results and discussion

In strong alkaline media, α-diketones react with acetone derivatives of general formula (II), that have at least one hydrogen atom on each α position, to form cyclopentenone derivatives. This procedure consists of two successive aldol reaction, followed by a single dehydration. Usually, the second potential dehydration does not occurs. Since it was reported by Japp and his coworkers,[18] this cyclisation procedure, has been frequently used for preparation of cyclopentenones.[19-21] We performed this reaction, using *p*-Cl- or *p*-Br- substituted benzils and acetone or its derivatives having methyl or phenyl substituents (Scheme 1).

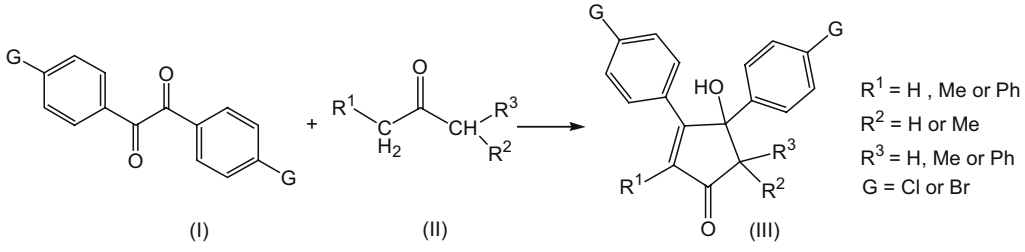
All reactions were performed at two different temperatures. At room temperature, reaction times varied from 1 to 18 hours (Table 1). These results suggesting that the reaction rates are significantly retarded in acetone derivatives which have one or two methyl substituents (entries 3, 7 and 8). At reflux temperature, the reaction times decrease as expected, except for reactions with α,α'-diphenylacetone (entries 5 and 10). Along with this general decrease in reaction times, a decrease in cyclopentenone yields also occurred (except for entries 1 and 4). Generally, the reaction yields for Br-substituted benzils are higher than Cl-substituted ones, either at room temperature or at reflux temperature; a quantitative yield was obtained from the reaction of 4,4'-dibromobenzil with the sterically less hindered acetone (entry 6).

After completion of the reaction, the major products were collected by filtration. By acidifying the alkaline residues, either *p,p'*-dicholorobenzilic acid (entries 1–5) or *p,p'*-dibromobenzilic acid (entries 6–10) were precipitated. The precipitates were identified by comparison of their melting points and IR spectra with authentic compounds.

*Spectroscopic identification*

The IR spectra of the cyclopentenones showed broad absorption for the hydroxyl groups ranging from 3256 to 3636 cm$^{-1}$, carbonyl absorption near 1700 cm$^{-1}$, and medium intensity bands of C=C near 1600 cm$^{-1}$. These are in accordance with previously reported values for 2-cyclopentene-1-one derivatives.[22] In $^1$H NMR spectra of cyclopentenone derivatives which possess a methylene moiety (entries 1, 2, 4, 6, 7 and 9) the two protons of methylene showed two doublets at high field with coupling constants ranging from 6 to 18 Hz. These doublets were used in the structure determination of compounds **(2)**, **(4)**, **(7)** and **(9)** which have two potential isomers (Scheme 2).

The presence of two doublets for the methylenes in the $^1$H NMR spectra of these compounds clearly indicates the selective formation of isomer **A** in each case, which is in accordance with Saytzeff's rule for elimination reactions. Another characteristic feature of these compounds is two




(I) (II) (III)

**Scheme 1** Condensation of substituted benzils and acetone derivatives via aldol reaction in alkaline media.

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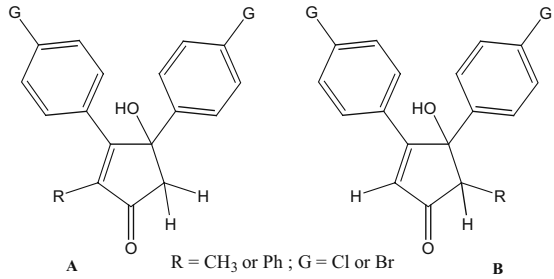



**Scheme 2** The two potential isomeric products expected for condensation of substituted benzils with asymmetric ketones.

or more doublets for *p*-di-substituted benzene rings in the aromatic region of the spectrum.

*Crystal structure of* $[C_{19}H_{16}Cl_2O_2]$ **(3)**

At the centre of title compound (**3**), five membered cyclopentenone ring has an envelope conformation (Fig. 1). The four carbon atoms of this ring, C(1), C(2), C(3) and C(4) are in a plane, and C(5) is 0.266 Å out of plane. The phenyl ring, C(12)–C(17), bonded to $sp^3$ carbon, C(4), has a dihedral angle of 65.12° to the main plane of the cyclopentenone ring. The other phenyl ring which is conjugated with enone system, has a tendency to be co-planar with this system, and is only rotated 21.83° from the main plane of cyclopentenone. This rotation probably resulted from the formation of intramolecular non classical C–H...O hydrogen bonding, from C(11)–H(11) to O(2) (Table 2). The internal angles of the five-membered ring ranged from 102.77(15)° for a $sp^3$ carbon, C(5), to 111.35(17)° for a $sp^2$ carbon, C(3). The bond distances also varied from 1.344(3)Å, for a double bond C–C, to 1.575(3) Å, for a single bond between two $sp^3$ carbon,

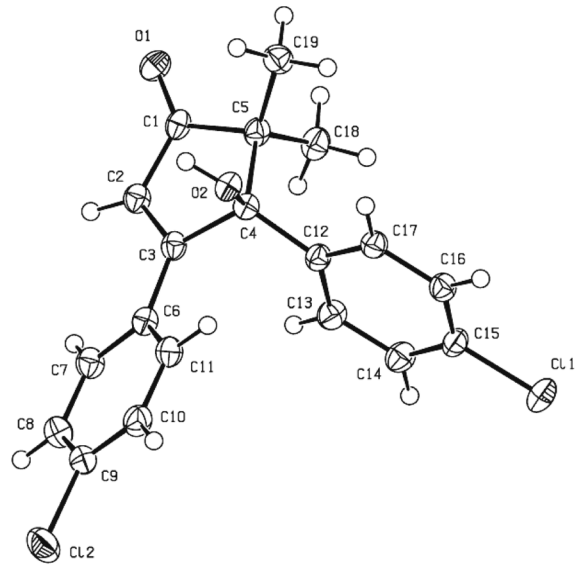



**Fig. 1** ORTEP view of **(3)** with displacement ellipsoids drown at 50% probability.

C(4)–C(5) (Table 3). These values are very close to that of previously reported structures.[23,24]

In the crystalline structure of **(3)**, each molecule is connected to a couple adjacent molecules by two equal hydrogen bonds from hydroxyl group of a molecule, to carbonyl group of other one (O(2)–H(2)...O(1); Table 2). O–H…O hydrogen bonds make a zigzag supramolecular chain along with the *c* crystallographic axis. These chains are linked each other by intermolecular C–H…O hydrogen bonds (C(17)–H(17)…O(2); Table 2), and

**Table 1** Summary of results, the yields are for separated products

| | | | | | RT | | Reflux | |
|---|---|---|---|---|---|---|---|---|
| Entry | G | $R^1$ | $R^2$ | $R^3$ | Time/min | Yield/% | Time/min | Yield/% |
| 1 | Cl | H | H | H | 60 | 56 | 35 | 78 |
| 2 | Cl | $CH_3$ | H | H | 120 | 38 | 30 | 25 |
| 3 | Cl | H | $CH_3$ | $CH_3$ | 1080 | 33 | 90 | 19 |
| 4 | Cl | $C_6H_5$ | H | H | 60 | 40 | 30 | 60 |
| 5 | Cl | $C_6H_5$ | H | $C_6H_5$ | 60 | 45 | 75 | 37 |
| 6 | Br | H | H | H | 150 | 95 | 10 | 90 |
| 7 | Br | $CH_3$ | H | H | 1080 | 83 | 180 | 40 |
| 8 | Br | H | $CH_3$ | $CH_3$ | 600 | 55 | 180 | 45 |
| 9 | Br | $C_6H_5$ | H | H | 60 | 75 | 60 | 60 |
| 10 | Br | $C_6H_5$ | H | $C_6H_5$ | 60 | 45 | 120 | 43 |

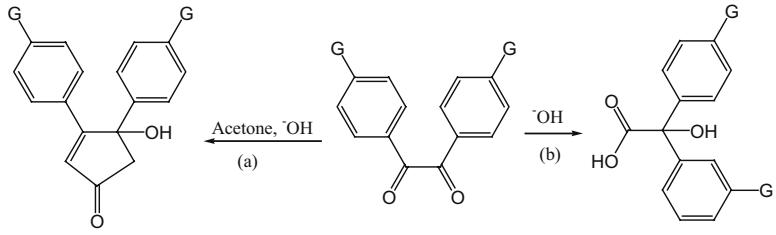
**Table 2** Hydrogen bonds for **(3)** [Å and°]

| D–H...A | d(D–H) | d(H...A) | d(D...A) | <(DHA) | type |
|---|---|---|---|---|---|
| O(2)–H(2)...O(1)# | 0.85 | 1.91 | 2.757(2) | 176 | Intermolecular |
| C(11)–H(11A)…O(2) | 0.95 | 2.43 | 3.035(2) | 121 | Intramolecular |
| C(17)–H(17A)…O(2)## | 0.95 | 2.54 | 3.378(2) | 147 | intermolecular |

Symmetry transformations used to generate equivalent atoms: # *x*,–*y* + 3/2; *z*–1/2, ## –*x*,1-*y*,–*z*

**Table 3** Selected bond lengths [Å] and angles [°] for **(3)**

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1.221(2) | O(2)–C(4) | 1.429(2) |
| C(1)–C(2) | 1.464(3) | C(1)–C(5) | 1.528(2) |
| C(2)–C(3) | 1.344(3) | C(3)–C(4) | 1.540(3) |
| C(4)–C(5) | 1.575(3) | C(5)–C(19) | 1.522(3) |
| O(1)–C(1)–C(2) | 127.22(17) | O(2)–C(4)–C(5) | 111.42(14) |
| O(2)–C(4)–C(12) | 106.73(14) | C(1)–C(5)–C(4) | 102.75(15) |
| C(2)–C(1)–C(5) | 108.52(16) | C(2)–C(3)–C(4) | 111.35(17) |
| C(2)–C(3)–C(6) | 125.94(17) | C(3)–C(2)–C(1) | 110.75(17) |
| C(3)–C(4)–C(5) | 103.44(14) | C(12)–C(4)–C(3) | 114.51(15) |
| C(18)–C(5)–C(4) | 113.28(15) | C(19)–C(5)–C(1) | 111.96(16) |




**Scheme 3** Competing reactions; aldol cyclisation (a) and benzil-benzilic acid rearrangement (b).

Cl(1)…Cl(2)[1–*x*, –0.5 + *y*, 0.5–*z*] close contacts (3.4146(8)Å; van der waals radii of two Cl atom 3.6 Å). This motif performs puckered sheets along with the *ab* crystallographic plane.

## Conclusion

Some of the above mentioned trends in the reaction times and yields of products, may be rationalised as a result of competition with a benzil-benzilic acid rearrangement.

The product of rearrangement may be found by acidifying the alkaline filtrates. This rearrangement is usual for α-diketones, especially aromatic ones, in strong alkaline media. The reaction is slower than the aldol condensation, but it is favoured by raising the temperature. Furthermore, electron-withdrawing substituents facilitate the migration of aryl groups and accelerate the benzil-benzilic acid rearrangement.[25] The competition causes a decrease in the yield of the aldol condensation products. Therefore, a decrease in the yield of cyclopentenone is observed at reflux temperature; and the yields of cyclopentenones derived from Cl-substituted benzils, are generally lesser than Br-substituted analogues. On the other hand, the aldol condensation is favoured by less bulky enolates; therefore the higher yields are obtained using acetone itself (Table 1, entries 1 and 6).

## Experimental

All chemicals were purchased from Merck or Fluka chemical companies, and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus, and are uncorrected. IR spectra were measured on a Shimadzu IR-460 spectrometer. NMR spectra were obtained from Bruker-Avance 300 MHz instrument using TMS as internal standard. Mass spectra were recorded on a Shimadzu GC/MS QP1100 EX model. Elemental analyses for the C and H were performed using a Heraeus CHN-O-Rapid analyser.

*Typical synthetic procedure (exemplified by entry 1)*

A solution of sodium hydroxide in methanol (2 ml, 10%) was added to a magnetically stirred mixture of 4,4'-dichlorobenzil (90 mg, 0.3 mmol) and acetone (120 mg, 2 mmol). The progress of the reaction was monitored by TLC. After 1 h stirring at room temperature, cold water (200 ml) was added to the mixture and the precipitate was filtered, washed successively with water and a mixture of hexane/ether, and dried in vacuo. After recrystallisation from toluene, colourless crystals of *3,4-bis(4-chloro phenyl)-4-hydroxy-2-cyclopentene-1-one* (**1**) (57 mg, 56%) were obtained. M.p. 229–230°C. Anal. Calcd for $C_{17}H_{12}Cl_2O_2$ (319.18): C, 64.0; H 3.8. Found: C, 64.4; H, 3.7%. IR (KBr)($\nu_{max}$, $cm^{-1}$): 3405 (OH), 1692 (C=O), 1542 (C=C). $^1$H NMR (acetone-$d_6$): δ 2.73 (1H, d, *J* = 18 Hz, methylene), 3.01 (1H, d, *J* = 18 Hz, methylene), 5.81 (1H, s, OH), 6.80 (1H, s, CH), 7.30 (4H, d, *J* = 8.7 Hz, $C_6H_4$), 7.43 (2H, d, *J* = 8.7 Hz, $C_6H_4$), 7.75 (2H, d, *J* = 8.7 Hz, $C_6H_4$). $^{13}$C NMR (acetone-$d_6$): δ 56.9, 81.4, 121.3, 125.2, 127.2, 129.4, 130.1, 131.8, 133.1, 136.6, 144.9, 172.5, 204. MS (m/z,%): 318 ($M^+$ ($^{35}$Cl), 42), 320 ($M^+$ ($^{37}$Cl), 20), 165 (60), 136 (100), 111 (70).

*3,4-Bis(4-chlorophenyl)-4-hydroxy-2-methyl-2-cyclopentene-1-one* (**2**): Slightly yellow crystals recrystallised from toluene solution. M.p. 98–101°C. Anal. Calcd for $C_{18}H_{14}Cl_2O_2$ (333.21): C, 64.9; H 4.2. Found: C, 64.5; H, 4.1%. IR (KBr)($\nu_{max}$, $cm^{-1}$): 3420 (OH), 1695 (C=O), 1594 (C=C). $^1$H NMR (acetone-$d_6$): δ 1.85 (3H, s, $CH_3$), 2.76 (1H, d, *J* = 12 Hz, methylene), 2.97 (1H, d, *J* = 12 Hz, methylene), 5.53 (1H, S, OH) 7.30 (2H, d, *J* = 8.6 Hz, $C_6H_4$), 7.33 (2H, d, *J* = 8.7 Hz, $C_6H_4$), 7.41 (2H, d, *J* = 8.6 Hz, $C_6H_4$), 7.43 (2H, d, *J* = 8.7 Hz, $C_6H_4$). $^{13}$C NMR (acetone-$d_6$): δ 9.8, 55.1, 80.9, 121, 123.2, 128.2, 131.7, 131.8, 132.1, 134.8, 138.4, 144.3, 167.3, 205.8. MS (*m/z*,%): 332 ($M^+$ ($^{35}$Cl),8), 334 ($M^+$ ($^{37}$Cl), 5), 193 (18), 195 (10), 149 (48), 139 (100), 115 (97), 112 (50), 43 (21), 42 (38).

*3,4-Bis(4-chlorophenyl)-5,5-dimethyl-4-hydroxy-2-cyclopentene-1-one* (**3**): Colourless crystals recrystallised from toluene solution. M.p. 162–164°C. Anal. Calcd for $C_{19}H_{16}Cl_2O_2$ (347.22): C, 65.7; H 4.6. Found: C, 65.7; H, 4.5%. IR (KBr)($\nu_{max}$, $cm^{-1}$): 3349 (OH), 1688 (C=O), 1594 (C=C). $^1$H NMR (acetone-$d_6$): δ 0.54 (3H, s, $CH_3$), 1.27 (3H, s, $CH_3$), 5.31 (1H, S, OH), 7.35 (4H, d, *J* = 8.9 Hz, $C_6H_4$), 7.72 (4H, d, *J* = 8.9 Hz, $C_6H_4$). $^{13}$C NMR (acetone-$d_6$): δ 21.8, 32.8, 55.8, 86.4, 128.2, 128.5, 128.9, 129.3, 132, 132.1, 133.4, 136.5, 142.6, 169.7, 209.4. MS (*m/z*,%): 331 (M-15, 15), 333 (6), 101 (39), 75 (50), 43 (42), 41 (100).

*3,4-Bis(4-chlorophenyl)-4-hydroxy-2-phenyl-2-cyclopentene-1-one* (**4**): Colourless crystals recrystallised from toluene solution. M.p. 142–143°C. Anal. Calcd for $C_{23}H_{16}Cl_2O_2$ (395.28): C, 69.9; H 4.1. Found: C, 69.4; H, 4.3%. IR (KBr)($\nu_{max}$, $cm^{-1}$): 3346 (OH), 1705 (C=O), 1597 (C=C). $^1$H NMR (acetone-$d_6$): δ 2.94 (1H, d, *J* = 18 Hz, methylene), 3.14 (1H, d, J = 18 Hz, methylene), 5.74 (1H, s, OH), 7.15–7.32 (9H, m, aromatic rings), 7.34 (2H, d, *J* = 8.7 Hz, $C_6H_4$), 7.54 (2H, d, *J* = 8.7 Hz $C_6H_4$). $^{13}$C NMR (acetone-$d_6$): δ 55.7, 80.4, 121.8, 124.1, 127.9, 128.8, 129, 129.2, 130.7, 132.1, 133.1, 133.5, 135, 141.1, 144.3, 168.2, 204. MS (*m/z*,%): 394 ($M^+$ ($^{35}$Cl), 10), 396 ($M^+$ ($^{37}$Cl), 5), 255 (10), 212 (62), 139 (100), 111 (95), 91 (48), 77 (50).

*3,4-Bis(4-chlorophenyl)-2, 5-diphenyl-4-hydroxy-2-cyclopentene-1-one* (**5**): Yellow crystals recrystallised from toluene solution. M.p. 350°C; Anal. Calcd for $C_{29}H_{20}Cl_2O_2$ (471.37): C, 73.9; H, 4.3. Found: C, 74.0; H, 4.2%. IR (KBr)($\nu_{max}$, $cm^{-1}$): 3636(OH), 1712 (C=O), 1664 (C=C). $^1$H NMR (acetone-$d_6$): δ 2.87 (1H, s, CH), 4.00 (1H, s, OH), 6.94–7.38 (18H, m, aromatic rings). $^{13}$C NMR (acetone-$d_6$): δ 56.2, 81.7, 120.3, 123.2, 128.6, 128.9, 129.2, 130.9, 131.5, 131.9, 132.8, 133.1, 133.5, 135, 154.3, 148.4, 142.3, 142.7, 144.6, 168.2, 202.1.

*3,4-Bis(4-bromophenyl)-4-hydroxy-2-cyclopentene-1-one* (**6**): Slightly yellow crystals recrystallised from toluene solution. M.p. 239–241°C. Anal. Calcd for $C_{17}H_{12}Br_2O_2$ (408.08): C, 50.0; H 3.0. Found: C, 49.7; H, 2.7%. IR (KBr)($\nu_{max}$, $cm^{-1}$): 3392(OH), 1679 (C=O), 1587 (C=C). $^1$H NMR (acetone-$d_6$): δ 2.73 (1H, d, *J* = 18 Hz, methylene), 2.98 (1H, d, *J* = 18 Hz, methylene), 5.89 (1H, s, OH), 6.81 (1H, s, CH), 7.43 (2H, d, *J* = 8.7 Hz, $C_6H_4$), 7.5 (4H, d, *J* = 8.7 Hz, $C_6H_4$), 7.72 (2H, d, *J* = 8.7 Hz, $C_6H_4$),. $^{13}$C NMR (acetone-$d_6$): δ 56.8, 81.5, 121.3, 125.2, 127.6, 130.2, 132, 132.4, 133.2, 136.6, 144.6, 171.8, 204.2. MS (*m/z*,%): 406 ($M^+$ ($^{79}Br_2$), 50), 408 (M + ($^{79}$Br $^{81}$Br), 85), 410 ($M^+$ ($^{81}Br_2$), 45), 209 (70), 211 (68), 183 (80), 185 (78), 144 (25), 101(30), 75 (32).

*3,4-Bis(4-bromophenyl)-4-hydroxy-2-methyl-2-cyclopentene-1-one* (**7**): Colourless crystals recrystallised from toluene solution. M.p. 167–169°C. Anal. Calcd for $C_{18}H_{14}Br_2O_2$ (422.11): C, 51.2; H 3.3. Found: C, 51.3; H, 3.4%. IR (KBr)($\nu_{max}$, $cm^{-1}$): 3442 (OH), 1685 (C=O), 1617 (C=C). $^1$H NMR (acetone-$d_6$): δ 1.85 (3H, s, $CH_3$), 2.85 (1H, d, *J* = 12 Hz, methylene), 2.95 (1H, d, *J* = 12 Hz, methylene), 5.53 (1H, s, OH), 7.34 (2H, d, *J* = 8.6 Hz, $C_6H_4$), 7.37 (2H, d, *J* = 8.7 Hz, $C_6H_4$), 7.44 (2H, d, *J* = 8.7, Hz $C_6H_4$), 7.48 (2H, d, *J* = 8.6 Hz, $C_6H_4$). $^{13}$C NMR (acetone-$d_6$): δ 9.7, 80.4, 80.4, 121.3, 123.3, 128.1, 131.8, 131.9, 132, 134.1, 138.9, 144.5, 167.1, 205.5. MS (*m/z*,%): 420 ($M^+$ ($^{79}Br_2$), 12), 422 ($M^+$ ($^{79}$Br $^{81}$Br), 31), 424 ($M^+$ ($^{81}Br_2$), 14), 313 (20), 315 (20), 183 (75), 185 (74), 115 (100).

*3,4-Bis(4-bromophenyl)-5,5-dimethyl-4-hydroxy-2-cyclopentene-1-one* (**8**): Colourless crystals recrystallised from toluene solution. M.p. 197–199°C. Anal. Calcd for $C_{19}H_{16}Br_2O_2$ (436.14): C, 52.3; H 3.7. Found: C, 52.1; H, 3.6%. IR (KBr)($\nu_{max}$, $cm^{-1}$): 3256 (OH), 1690 (C=O), 1601(C=C). $^1$H NMR (acetone-$d_6$): δ 0.54 (3H, s, $CH_3$), 1.27 (3H, s, $CH_3$), 5.39 (1H, s, OH), 6.81 (1H, s, CH), 7.5 (4H, d, *J* = 8.7 Hz, $C_6H_4$), 7.65(4H, d, *J* = 8.7 Hz, $C_6H_4$). $^{13}$C NMR (acetone-$d_6$): δ 21.8, 32.9, 55.6, 86.2, 128.2, 128.6, 128.2, 129.1, 133.1, 136.6,

142.1, 142.6, 168.9, 169.7, 209.4. MS (*m/z*,%): 434 ($M^+$ ($^{79}Br_2$), 25), 436 (M + ($^{79}Br$ $^{81}Br$), 50), 438 ($M^+$ ($^{81}Br_2$), 27), 437 (24), 419 (100), 421 (100), 419 (80), 286 (25), 288 (25), 183 (25), 185 (25), 155 (15), 157 (13).

*3,4-Bis(4-bromophenyl)-4-hydroxy-2-phenyl-2-cyclopentene-1-one* (**9**): Yellow crystals recrystallised from toluene solution. M.p. 160–162°C. Anal. Calcd for $C_{23}H_{16}Br_2O_2$ (484.18): C, 57.05; H 3.3. Found: C, 56.3; H, 3.2%. IR (KBr)($\nu_{max}$, $cm^{-1}$): 3438 (OH), 1701 (C=O), 1599 (C=C); $^1H$ NMR (acetone-$d_6$): δ 2.90 (1H, d, *J* = 6 Hz, methylene), 3.02 (1H, d, *J* = 6 Hz, methylene), 5.76 (1H, s, OH), 7.1–7.48 (13H, m, aromatic rings). $^{13}C$ NMR (acetone-$d_6$): δ 55.7, 80.4, 121.3, 123.4, 128.3, 128.9, 129, 130.7, 131.8, 132.2, 132.3, 132.6, 134, 141.3, 144.8, 168.2, 203.6. MS(*m/z*,%): 482($M^+$($^{79}Br_2$),52), 484(M + ($^{79}Br$ $^{81}Br$), 100), 486($M^+$($^{81}Br_2$), 52), 256(75), 258(74), 176(80), 151(40), 77(25).

*3,4-Bis(4-bromophenyl)-2,5-diphenyl-4-hydroxy-2-cyclopentene-1-one* (**10**): Colourless crystals recrystallised from toluene solution. M.p. 277–279°C. Anal. Calcd for $C_{29}H_{20}Br_2O_2$ (560.28): C, 62.2; H, 3.6. Found: C, 62.3; H, 3.55%. IR (KBr) ($\nu_{max}$, $cm^{-1}$): 3407 (OH), 1717 (C=O), 1664 (C=C). $^1H$ NMR (acetone-$d_6$): δ 2.86 (1H, s, CH), 4.00 (1H, s, OH), 6.87–7.37 (18H, m, aromatic rings). $^{13}C$ NMR (acetone-$d_6$): δ 56.1, 81.5, 120.7, 123.1, 128.4, 128.8, 129.1, 131.1, 131.6, 131.6, 132.9, 133.3, 133.6, 135.1, 154.5, 148.5, 142.6, 142.7, 144.8, 168.1, 202.3.

*X-ray crystallography*

Diffraction data were collected on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å). A total of 17171 reflections were collected, which reduced to 4044 unique reflections ($R_{int}$ = 0.028). The structure was solved by direct methods, and refined on $F^2$ using all data by Full-matrix least-square procedures using SHELXTL ver. 5.1 programs.[26] The hydrogen atoms of OH groups were found in the difference Fourier synthesis. The H(C) atom positions were calculated. Crystallographic data for **(3)** are as follows: $C_{19}H_{16}Cl_2O_2$, molecular weight 347.22, monoclinic, $P2_1/c$, $a$ = 13.3780(9), $b$ = 17.6225(12), $c$ = 7.2561 (5) Å, $\beta$ = 100.938(2)°, $V$ = 1682.4(2) $Å^3$, $Z$ = 4, $T$ = 120(2) K, $F(000)$ = 720, μ = 0.39 $mm^{-1}$, $D_{calc}$ = 1.371 Mg $m^{-3}$, $2\theta_{max}$ = 55.90°, 208 parameters, Goodness-of-fit = 1.034, $wR(F^2)$ = 0.0988 (all data), $wR(F^2)$ = 0.9225 (1634 data with $I > 2\sigma I$), $R$ = 0.0607 (all data), $R$ = 0.0500 (1634 data with $I > 2\sigma I$).

*Supplementary data*

CCDC 676615 contains the supplementary crystallographic data of this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif.

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