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# of 1-alkylamino-5 enzoylcyclopenta-
# in the THF/$H_2O$ system

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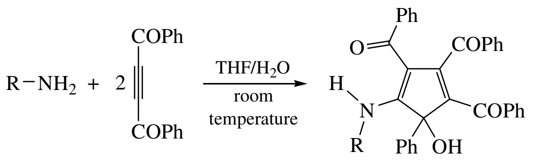
**The reaction of one equivalent of primary amines with two equivalents of dibenzoylacetylene in the THF/$H_2O$ system leads to 1-alkylamino-5-hydroxy-5-phenyl-2,3,4-tribenzoylcyclopenta-1,3-dienes in good yields.**

The synthesis and synthetic applications of multifunctional cyclopentadienes have been widely investigated.[1–4] In spite of the extensive development in the chemistry of cyclopentadienyl ligands, little attention has been paid to the synthesis of fully substituted cyclopentadienes.[5,6] The reaction of primary amines with acetylenic esters has been discussed.[7–9] The products of these reactions are *cis* and *trans* isomers of the related enaminines. As a part of our studies on heterocyclic and carbocyclic systems,[10] we now report a convenient and facile preparation of fully substituted cyclopentadienes using primary amines **1** and dibenzoylacetylene (DBA) in 1:1 THF/$H_2O$ as a solvent. This reaction produces 1-alkylamino-5-hydroxy-5-phenyl-2,3,4-tribenzoylcyclopenta-1,3-dienes **2** in good yields† (Scheme 1).

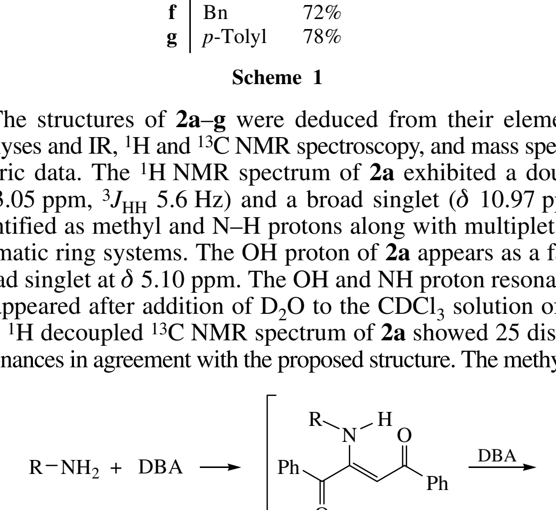


**1a–g** DBA **2a–g**

| | R | Yield of **2** |
|---|---|---|
| **a** | Me | 75% |
| **b** | Et | 78% |
| **c** | Pr | 80% |
| **d** | Bu | 75% |
| **e** | Allyl | 70% |
| **f** | Bn | 72% |
| **g** | *p*-Tolyl | 78% |

**Scheme 1**

The structures of **2a**–**g** were deduced from their elemental analyses and IR, $^1H$ and $^{13}C$ NMR spectroscopy, and mass spectrometric data. The $^1H$ NMR spectrum of **2a** exhibited a doublet ($\delta$ 3.05 ppm, $^3J_{HH}$ 5.6 Hz) and a broad singlet ($\delta$ 10.97 ppm), identified as methyl and N–H protons along with multiplets for aromatic ring systems. The OH proton of **2a** appears as a fairly broad singlet at $\delta$ 5.10 ppm. The OH and NH proton resonances disappeared after addition of $D_2O$ to the $CDCl_3$ solution of **2a**. The $^1H$ decoupled $^{13}C$ NMR spectrum of **2a** showed 25 distinct resonances in agreement with the proposed structure. The methylene protons of the benzyl group in **2f** are diastereotopic and exhibit an ABX system ($J_{AB}$ 15.1 Hz, $J_{AX} = J_{BX}$ = 5.0 Hz, $\delta_A$ 4.56, $\delta_B$ 4.62 ppm). The mass spectra of compounds **2a**–**g** displayed molecular ion peaks at appropriate *m*/*z* values.



**Scheme 2**

A possible mechanism for the formation of **2** is proposed in Scheme 2. The reaction involves the sequence of two Michael additions of the primary amine to the electron-deficient acetylenic ketone to produce enaminocarbonyl compound **4**. Such an addition product may undergo cyclization under the reaction conditions employed to produce imine derivative **5**, which undergoes an imine-to-enamine tautomerism to generate highly functionalised cyclopentadiene **2**.

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† Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. Mass spectra were recorded on a Finnigan-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. The NMR spectra were recorded at 500.1 ($^1H$) and 125.7 ($^{13}C$) MHz on a Bruker Avance DRX-500 MHz NMR instrument with $CDCl_3$ as a solvent. Chemical shifts ($\delta$) are reported relative to TMS as an internal standard.

*Typical experimental procedure for the preparation of 5-hydroxy-1-methylamino-5-phenyl-2,3,4-tribenzoylcyclopenta-1,3-diene* **2a**. 0.16 g (40%) of methylamine (2 mmol) was added to a stirred solution of 0.94 g dibenzoylacetylene (4 mmol) in 10 ml of THF and 10 ml of $H_2O$ at room temperature. The reaction mixture was then stirred for 12 h. The precipitate was filtered off and crystallised in *n*-hexane–EtOAc. Product **2a** was obtained as yellow crystals, yield 0.75 g (75%), mp 178–180 °C. IR (KBr, $\nu$/cm$^{-1}$): 3418 (OH), 3230 (NH), 1654–1630 (C=O) and 1620–1590 (Ph). $^1H$ NMR, $\delta$: 3.05 (d, 3H, NMe, $^3J_{HH}$ 5.6 Hz), 5.26 (br. s, 1H, OH), 6.86–7.72 (m, 20H, Ar), 10.97 (br. s, 1H, NH···O=C). $^{13}C$ NMR, $\delta$: 31.5 (NMe), 85.8 (COH), 108.1 (N–C=*C*), 124.6, 126.9, 127.5, 127.6, 127.8, 128.1, 128.2, 128.3, 128.4, 128.9, 129.3 and 131.7 (19CH), 130.6 (C), 133.2 (CH), 136.7, 138.0, 138.9, 140.6 and 153.9 (5C), 178.4 (N–*C*=C), 192.2, 192.4 and 194.5 (3C=O). MS, *m*/*z* (%): 499 ($M^+$, 3), 394 (5), 105 (100), 77 (95). Found (%): C, 79.73; H, 5.09; N, 2.78. Calc. for $C_{33}H_{25}NO_4$ (499.6) (%): C, 79.34; H, 5.04; N, 2.80.

*For 5-hydroxy-1-ethylamino-5-phenyl-2,3,4-tribenzoylcyclopenta-1,3-diene* **2b**: light yellow crystals, yield 0.80 g (78%), mp 190–192 °C. IR (KBr, $\nu$/cm$^{-1}$): 3420 (OH), 3205 (NH), 1674–1635 (C=O), 1620–1590 (Ph). $^1H$ NMR, $\delta$: 1.10 (t, 3H, Me, $^3J_{HH}$ 7.2 Hz), 3.52 (m, 2H, $NCH_2$), 6.35 (br. s, 1H, OH), 6.88–7.82 (m, 20H, Ar), 10.98 (br. s, 1H, NH···O=C). $^{13}C$ NMR, $\delta$: 14.8 (Me), 39.8 ($CH_2$), 85.6 (COH), 107.6 (N–C=*C*), 124.6, 127.0, 127.6, 127.7, 128.1, 128.2, 128.3, 128.4, 129.0 and 129.9 (18CH), 130.1 (C), 131.8 and 133.3 (2CH), 136.9, 138.9, 139.2, 140.8 and 154.1 (5C), 177.8 (N–*C*=C), 192.6, 192.9 and 195.0 (3C=O). MS, *m*/*z* (%): 513 ($M^+$, 4), 408 (3), 122 (10), 105 (100), 77 (75). Found (%): C, 79.22; H, 5.35; N, 2.77. Calc for $C_{34}H_{27}NO_4$ (513.6) (%): C, 79.51; H, 5.30; N, 2.73.

*For 5-hydroxy-1-propylamino-5-phenyl-2,3,4-tribenzoylcyclopenta-1,3-diene* **2c**: yellow crystals, yield 0.84 g (80%), mp 212–214 °C. IR (KBr, $\nu$/cm$^{-1}$): 3428 (OH), 3210 (NH), 1664–1634 (C=O) and 1627–1590 (Ph). $^1H$ NMR, $\delta$: 0.79 (t, 3H, Me, $^3J_{HH}$ 7.3 Hz), 1.27 and 1.43 (2m, 2H, $CH_2$), 3.39 and 3.56 (2m, 2H, $NCH_2$), 6.83–7.71 (m, 21H, Ar and OH), 11.05 (br. s, 1H, NH···O=C). $^{13}C$ NMR, $\delta$: 10.9 (Me), 23.1 ($CH_2$), 46.6 ($NCH_2$), 85.6 (COH), 107.7 (N–C=*C*), 124.5, 126.9, 127.5, 127.6, 128.0, 128.2, 128.3, 128.8, 129.8 and 131.7 (18CH), 130.1 (C), 131.7 and 133.2 (2CH), 136.7, 138.8, 139.0, 140.6 and 153.9 (5C), 177.7 (N–*C*=C), 192.4, 192.5 and 193.3 (3C=O). MS, *m*/*z* (%): 528 ($M^+$ + 1, 2), 105 (100), 77 (85), 51 (40). Found (%): C, 79.34; H, 5.58; N, 2.68. Calc. for $C_{35}H_{29}NO_4$ (527.6) (%): C, 79.68; H, 5.54; N, 2.65.

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This reaction of primary amines with dibenzoylacetylene in the THF/$\mathrm{H_2O}$ system provides a simple one-pot entry into the synthesis of 1-alkylamino-5-hydroxy-5-phenyl-2,3,4-tribenzoylcyclopenta-1,3-dienes of potential synthetic interest.

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*For 5-hydroxy-1-butylamino-5-phenyl-2,3,4-tribenzoylcyclopenta-1,3-diene* **2d**: yellow crystals, yield 0.81 g (75%), mp 154–156 °C. IR (KBr, $\nu$/cm$^{-1}$): 3412 (OH), 3204 (NH), 1672–1636 (C=O), 1630–1592 (Ph). $^{1}$H NMR, $\delta$: 0.79 (t, 3H, Me, $^{3}J_{\mathrm{HH}}$ 6 Hz), 1.20–1.43 (m, 4H, 2$\mathrm{CH_2}$), 3.42 and 3.58 (2m, 2H, $\mathrm{NCH_2}$), 5.82 (br. s, 1H, OH), 6.82–7.71 (m, 20H, Ar), 11.04 (br. s, 1H, NH···O=C). $^{13}$C NMR, $\delta$: 13.4 (Me), 19.6 and 31.8 (2$\mathrm{CH_2}$), 44.8 ($\mathrm{NCH_2}$), 85.6 (COH), 107.7 (N–C=*C*), 124.6, 126.9, 127.5, 127.6, 127.8, 128.0, 128.1, 128.2, 128.3, 128.8 and 129.8 (18CH), 129.9 (C), 131.7 and 133.1 (2CH), 136.7, 138.7, 139.0, 140.6, and 153.9 (5C), 177.6 (N–*C*=C), 192.3, 192.4 and 194.6 (3C=O). MS, *m*/*z* (%): 542 ($\mathrm{M^+}$ + 1, 2), 105 (100), 77 (85), 51 (35). Found (%): C, 80.12; H, 5.74; N, 2.62. Calc. for $\mathrm{C_{36}H_{31}NO_4}$ (541.6) (%): C, 79.83; H, 5.77; N, 2.59.

*For 5-hydroxy-1-allylamino-5-phenyl-2,3,4-tribenzoylcyclopenta-1,3-diene* **2e**: yellow crystals, yield 0.74 g (70%), mp 172–174 °C. IR (KBr, $\nu$/cm$^{-1}$): 3405 (OH), 3212 (NH), 1674–1636 (C=O), 1630–1590 (Ph). $^{1}$H NMR, $\delta$: 4.04 and 4.18 (2m, 2H, $\mathrm{NCH_2}$), 5.05 (m, 2H, =$\mathrm{CH_2}$), 5.51 (m, 1H, HC=), 6.25 (br. s, 1H, OH), 6.84–7.70 (m, 20H, Ar), 10.93 (br. s, 1H, NH···O=C). $^{13}$C NMR, $\delta$: 47.4 ($\mathrm{NCH_2}$), 85.8 (COH), 108.0 (N–C=*C*), 118.1 (=$\mathrm{CH_2}$), 124.6, 127.0, 127.5, 127.6, 128.1, 128.2, 128.3, 128.4, 129.0 and 129.9 (18CH), 130.3 (C), 131.8, 132.3 and 133.2 (3CH), 136.7, 138.6, 139.0, 140.6 and 153.6 (5C), 177.2 (N–*C*=C), 192.4, 192.5 and 194.6 (3C=O). MS, *m*/*z* (%): 525 ($\mathrm{M^+}$, 3), 420 (5), 105 (100), 77 (98), 57 (30). Found (%): C, 80.43; H, 5.22; N, 2.63. Calc. for $\mathrm{C_{35}H_{27}NO_4}$ (525.6) (%): C, 79.98; H, 5.18; N, 2.66.

*For 5-hydroxy-1-benzylamino-5-phenyl-2,3,4-tribenzoylcyclopenta-1,3-diene* **2f**: yellow crystals, yield 0.83 g (72%), mp 103–105 °C. IR (KBr, $\nu$/cm$^{-1}$): 3424 (OH), 3280 (NH), 1665–1635 (C=O), 1630–1592 (Ph). $^{1}$H NMR, $\delta$: 4.59 (ABX system, $\delta_{\mathrm{A}}$ 4.56, $\delta_{\mathrm{B}}$ 4.62, 2H, $\mathrm{NCH_2}$, $J_{\mathrm{AB}}$ 15.0 Hz, $J_{\mathrm{AX}} = J_{\mathrm{BX}} = 5$ Hz), 6.75 (br. s, 1H, OH), 6.88–7.83 (m, 25H, Ar), 11.20 (br. s, 1H, NH···O=C). $^{13}$C NMR, $\delta$: 49.1 ($\mathrm{NCH_2}$), 86.0 (COH), 108.4 (N–C=*C*), 125.0, 127.4, 128.0, 128.2, 128.4, 128.5, 128.6, 128.8, 129.2, 129.5 and 130.4 (23CH), 130.7 (C), 132.2 and 133.7 (2CH), 136.2, 137.2, 139.1, 139.4, 141.0 and 154.2 (6C), 177.6 (N–*C*=C), 193.1, 193.3 and 195.6 (3C=O). MS, *m*/*z* (%): 575 ($\mathrm{M^+}$, 10), 467 (8), 105 (100), 77 (75). Found (%): C, 81.85; H, 5.12; N, 2.46. Calc. for $\mathrm{C_{39}H_{29}NO_4}$ (575.7) (%): C, 81.37; H, 5.08; N, 2.43.

*For 5-hydroxy-1-(4-methylphenyl)amino-5-phenyl-2,3,4-tribenzoylcyclopenta-1,3-diene* **2g**: yellow crystals, yield 0.90 g (78%), mp 182–184 °C. IR (KBr, $\nu$/cm$^{-1}$): 3456 (OH), 3168 (NH), 1674–1638 (C=O), 1631–1595 (Ph). $^{1}$H NMR, $\delta$: 2.30 (s, 3H, Me), 6.27 (br. s, 1H, OH), 6.85–7.43 (m, 24H, Ar), 12.54 (br. s, 1H, NH···O=C). $^{13}$C NMR, $\delta$: 21.0 (Me), 86.3 (COH), 109.0 (N–C=*C*), 124.6, 125.7, 127.1, 127.6, 127.7, 128.0, 128.1, 128.2, 128.4 and 128.7 (20CH), 130.3 (CH), 131.7 (C), 132.0 (CH), 133.2 (CH), 133.4 (C), 136.9 (C), 137.1 (CH), 137.2, 138.9, 140.5 and 152.5 (5C), 174.8 (N–*C*=C), 192.4, 193.0 and 195.0 (3C=O). MS, *m*/*z* (%): 575 ($\mathrm{M^+}$, 8), 105 (100), 91 (20), 77 (80). Found (%): C, 81.78; H, 5.13; N, 2.50. Calc. for $\mathrm{C_{39}H_{29}NO_4}$ (575.7) (%): C, 81.37; H, 5.08; N, 2.43.