Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Communications
Mendeleev Commun., 2006, **16(5)**, 275–276

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

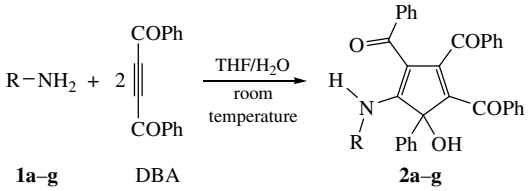
Issa Yavari*[a] and Farough Nasiri[b]

[a] *Department of Chemistry, Tarbiat Modarres University, 14115-175, Tehran, Iran. Fax: +98 21 8800 6544; e-mail: yavarisa@modares.ac.ir*
[b] *Department of Chemistry, University of Kurdistan, 416 Sanandaj, Iran*

DOI: 10.1070/MC2006v016n05ABEH002284

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).

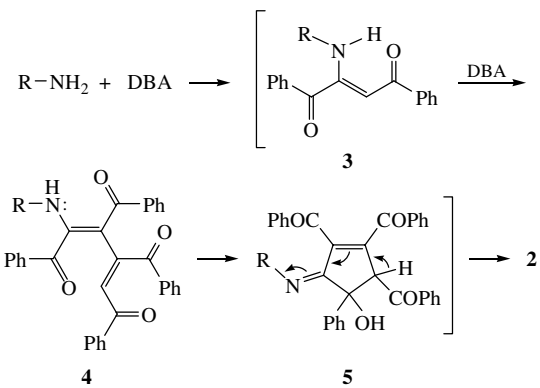


1a–g DBA **2a–g**

	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, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometric data. The ^{1}H NMR spectrum of **2a** exhibited a doublet (δ 3.05 ppm, $^3J_{HH}$ 5.6 Hz) and a broad singlet (δ 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 δ 5.10 ppm. The OH and NH proton resonances disappeared after addition of D_2O to the $CDCl_3$ solution of **2a**. The ^{1}H 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, δ_A 4.56, δ_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**.

† 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 (^{1}H) and 125.7 (^{13}C) MHz on a Bruker Avance DRX-500 MHz NMR instrument with $CDCl_3$ as a solvent. Chemical shifts (δ) 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, ν/cm^{-1}): 3418 (OH), 3230 (NH), 1654–1630 (C=O) and 1620–1590 (Ph). ^{1}H NMR, δ: 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, δ: 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, ν/cm^{-1}): 3420 (OH), 3205 (NH), 1674–1635 (C=O), 1620–1590 (Ph). ^{1}H NMR, δ: 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, δ: 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, ν/cm^{-1}): 3428 (OH), 3210 (NH), 1664–1634 (C=O) and 1627–1590 (Ph). ^{1}H NMR, δ: 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, δ: 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.

This reaction of primary amines with dibenzoylacetylene in the THF/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.

References

1 J. Christoffers, T. Werner, A. Baro and P. Fischer, *J. Organomet. Chem*., 2004, **689**, 3550 and references therein.
2 D. Mendez, E. Klimova, T. Klimova, O. S. Hernandez and G. M. Martinez, *J. Organomet. Chem.*, 2003, **681**, 115.
3 W. J. Evans, D. G. Giaricos and J. W. Ziller, *J. Organomet. Chem*., 2003, **688**, 200.
4 E. Aqad, P. Leriche, G. Mabon, A. Gorgues, M. Allain, A. Riou, A. Ellern and V. Khodorkovsky, *Tetrahedron*, 2003, **59**, 5773.
5 V. Nair, R. S. Menon, P. B. Beneesh, V. Sreekumar and S. Bindu, *Org. Lett*., 2004, **6**, 767.
6 H. Fang, Q. Song, Z. Wang and Z. Xi, *Tetrahedron Lett*., 2004, **45**, 5159.
7 K. Herbig, R. Huisgen and H. Huber, *Chem. Ber.*, 1966, **99**, 2546.
8 E. Czerwiska, L. Kozerski and J. Boksa, *Org. Magn. Reson*., 1976, **8**, 345.
9 (*a*) I. Yavari and A. Hosain-Nia, *Magn. Reson. Chem*., 1992, **30**, 413; (*b*) I. Yavari, A. Shaabani, H. Soleimani, F. Nourmohammadian and H. R. Bijanzadeh, *Magn. Reson. Chem*., 1996, **34**, 1003.

Received: 1st December 2005; Com. 05/2626

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, ν/cm^{-1}): 3412 (OH), 3204 (NH), 1672–1636 (C=O), 1630–1592 (Ph). ^{1}H NMR, δ: 0.79 (t, 3H, Me, $^3J_{HH}$ 6 Hz), 1.20–1.43 (m, 4H, 2CH_2), 3.42 and 3.58 (2m, 2H, 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, δ: 13.4 (Me), 19.6 and 31.8 (2CH_2), 44.8 (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 (M^+ + 1, 2), 105 (100), 77 (85), 51 (35). Found (%): C, 80.12; H, 5.74; N, 2.62. Calc. for $C_{36}H_{31}NO_4$ (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, ν/cm^{-1}): 3405 (OH), 3212 (NH), 1674–1636 (C=O), 1630–1590 (Ph). ^{1}H NMR, δ: 4.04 and 4.18 (2m, 2H, NCH_2), 5.05 (m, 2H, =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, δ: 47.4 (NCH_2), 85.8 (COH), 108.0 (N–C=*C*), 118.1 (=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 (M^+, 3), 420 (5), 105 (100), 77 (98), 57 (30). Found (%): C, 80.43; H, 5.22; N, 2.63. Calc. for $C_{35}H_{27}NO_4$ (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, ν/cm^{-1}): 3424 (OH), 3280 (NH), 1665–1635 (C=O), 1630–1592 (Ph). ^{1}H NMR, δ: 4.59 (ABX system, δ_A 4.56, δ_B 4.62, 2H, NCH_2, J_{AB} 15.0 Hz, J_{AX} = J_{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, δ: 49.1 (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 (M^+, 10), 467 (8), 105 (100), 77 (75). Found (%): C, 81.85; H, 5.12; N, 2.46. Calc. for $C_{39}H_{29}NO_4$ (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, ν/cm^{-1}): 3456 (OH), 3168 (NH), 1674–1638 (C=O), 1631–1595 (Ph). ^{1}H NMR, δ: 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, δ: 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 (M^+, 8), 105 (100), 91 (20), 77 (80). Found (%): C, 81.78; H, 5.13; N, 2.50. Calc. for $C_{39}H_{29}NO_4$ (575.7) (%): C, 81.37; H, 5.08; N, 2.43.