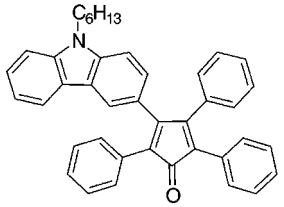
Improved Synthesis of Unsymmetrical, Heteroaromatic 1,2-Diketones and the Synthesis of Carbazole Ring Substituted Tetraaryl Cyclopentadieneones

Christopher J. Walsh† and Braja K. Mandal*

Department of Biological, Chemical, and Physical Sciences, Illinois Institute of Technology, 3255 South Dearborn, Chicago, Illinois 60616

Received March 9, 1999

Substituted cyclopentadieneones have received much interest lately, functioning as important building blocks in several new syntheses of polyaromatic materials.[1] For instance, tetraarylcyclopentadieneones (tetracyclones) have been employed extensively in the preparation of large graphite disks.[2] Diarylcyclopentadieneones have been used to prepare soluble, blue light-emitting PPV-type polymers[3] and in the synthesis of corranulene,[4] a C_{60} buckyball fragment. In our laboratory, alkoxy derivatives of tetracyclone have been utilized to make soluble polyphenylated phthalocyanines for nonlinear optical (NLO) applications.[5] Since these polyaromatic materials exhibit useful properties, we wished to extend our studies to tetracyclone systems incorporating heteroaromatic ring moieties, especially those containing a carbazole ring, such as tetracyclone **1**.[6] Materials containing carbazole



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moieties are attractive for xerographic,[7] photorefractive,[8] and light-emitting applications[9] due to their superior charge-transport properties. In this paper, we report an improved and convenient preparation of unsymmetrical 1,2-diketones needed to prepare heteroaromatic ring substituted tetracyclones, such as **1**, and the use of **1** as a diene in a Diels−Alder cycloaddition reaction.

Tetracyclones are usually prepared by condensation of a 1,2-diketone with a 1,3-diaryl acetone derivative. As seen in Scheme 1, a convenient synthesis of **1** relies on an efficient preparation of the unsymmetrical 1,2-diketone **5**. Unsymmetrical 1,2-diketones have been prepared in high yield by the controlled oxidation of alkynes by a variety of reagents.[10] While permanganate oxidation[11] was most attractive, due to the availabilty of the starting materials and ease of workup, it had not been used on alkynes substituted with heterocyclic moieties such as pyridine or thiophene.[12] We were pleased to find that when alkyne **4**, prepared by Pd-catalyzed coupling[13] of 9-hexyl-3-iodocarbazole[14] with phenylacetylene, was treated with permanganate in neutral, buffered aqueous acetone, a 96% yield of the new diketone 1-[3-(9-hexyl)-carbazoyl]-2-phenylethane-1,2-dione, **5**, was obtained.

The success of the permanganate oxidation prompted us to study the suitability of the reaction with alkynes substituted by other heteroaromatic moieties, including pyridine and thiophene. A variety of known heteroaromatic ring-substituted unsymmetrical alkynes were prepared in high yields from readily available brominated heteroaromatics using conditions similar to those for alkyne **4** (Table 1).[13] The alkynes then reacted smoothly with permanganate in neutral aqueous acetone to give the 1,2-diketones in good to excellent yields. The electron-rich carbazole and thiophenes worked well (Table 1, entries 1−3) and gave high yields of both coupled and oxidized products. The pyridine derivatives gave slightly lower yields in the oxidation reaction. When the phenyl ring was replaced with a strong electron-withdrawing phthalonitrile ring, no 1,2-diketone was observed (Table 1, entry 6). Therefore, this method appears unsuitable for strong electron-withdrawing aromatic or heteroaromatic substituted alkynes. We believe that this two-step (alkyne coupling and controlled oxidation) methodology to prepare heteroaromatic ring-substituted unsymmetrical 1,2-diketones offers distinct advantages over other methods previously reported, such as the mixed "benzoin-type" condensation followed by oxidation,[6a,d] the SeO_2 oxidation of benzylic ketones or internal alkynes,[15] reaction of organometallic reagents with 1,4-dialkylpiperazine-2,3-diones,[16] and the reaction of acyl anion equiva-

† Kilpatrick Pre-Doctoral Fellow, IIT, 1998−1999.

(1) See, for example: (a) Morgenroth, F.; Berresheim, A. J.; Wagner M.; Müllen, K. *J. Chem. Soc., Chem. Commun.* **1998**, 1139. (b) Kübel, C.; Chen, S. L.; Müllen, K. *Macromolecules* **1998**, *31*, 6014. (c) Haag, R.; Ohlhorst, B.; Noltenmeyer, M.; Fleischer, R.; Stalke, D.; Schuster, A.; Kuck, D.; de Meijere, A. *J. Am. Chem. Soc.* **1995**, *117*, 10474. (d) Kumar, U.; Neenan, T. X. *Macromolecules* **1995**, *28*, 124.

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(11) Srinivasan, N. S.; Lee, D. G. *J. Org. Chem.* **1979**, *44*, 1574.

(12) For an example with furan, see: Holland, S.; Epsztein, R. *Bull. Chim. Soc. Fr.* **1971**, 1694.

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10.1021/jo9904213 CCC: $18.00
Published on Web 07/14/1999

Scheme 1

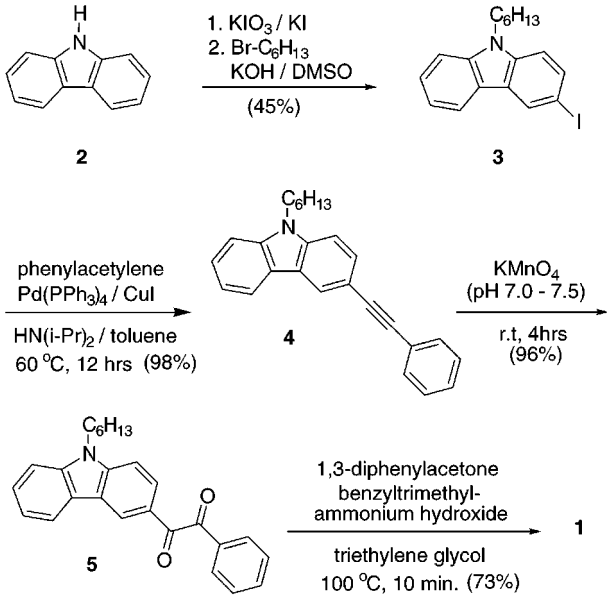
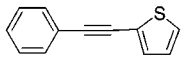
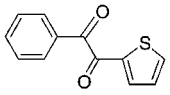
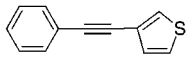
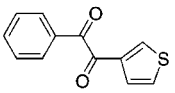
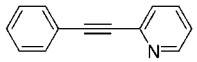
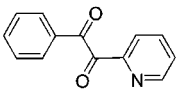
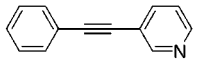
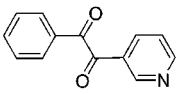
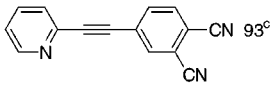


Table 1. Yields for the Synthesis of Coupled Alkynes and 1,2-Diketones

Entry	Alkyne	Yield[a] (%)	1,2-Diketone	Yield (%)
1	**4**	98[b]	**5**	96
2		80		90
3		84		88
4		92		55
5		88		73
6		93[c]	-	-[d]

[a] Yield of coupling between bromo-aromatic and phenylacetylene. [b] 3-Iodo-9-hexylcarbazole was used. [c] Yield of coupling between 4-iodophthalonitrile and 2-ethynylpyridine. [d] No 1,2-diketone was observed.

lents with acyl chlorides.[17] All of these methods have limitations when applied to pyridine or thiophene, such as low yields, the use of harsh conditions,[15] or symmetrical byproducts.[16] The 1,2-diketone **5** was then condensed with 1,3-diphenylacetone in triethylene glycol using benzyltrimethylammonium hydroxide as catalyst to produce the heteroaromatic ring substituted tetracyclone **1** (Scheme 1) in 73% yield.

Cyclic voltammetry and electronic absorption spectroscopy have been used to study substitutent effects in cyclopentadieneones.[6b,18] The cyclic voltammogram of **1** is shown in Figure 1. Two pseudoreversible reduction

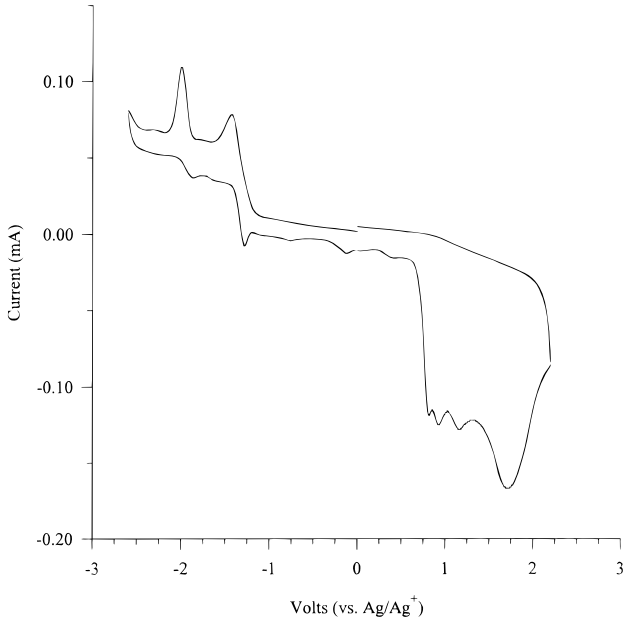


Figure 1. Cyclic voltammogram of **1**: 5×10^{-3} M in acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate; room temperature; scan rate 100 mV/s; glassy carbon working electrode; platinum wire counter electrode.

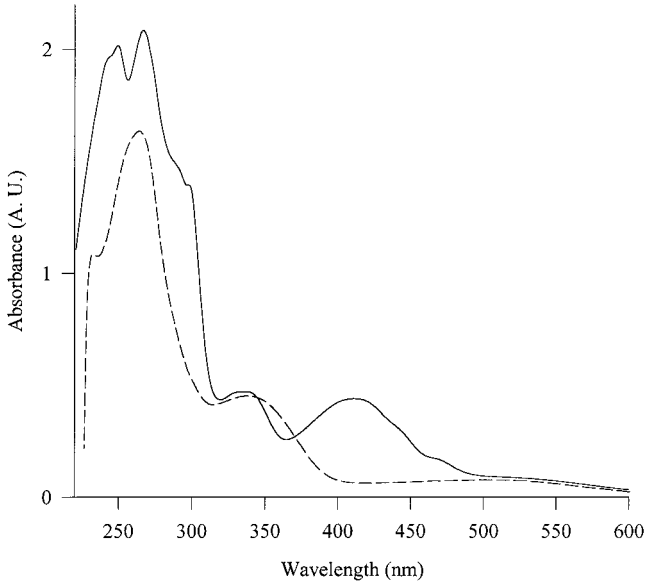


Figure 2. Electronic absorption spectra of **1** (solid line) and tetracyclone (dashed line) in CH_2Cl_2.

potentials of **1** occur at −1.25 and −1.80 V, compared with −1.15 and −1.75 V for unsubstituted tetracylone. The onset of several irreversible oxidations of **1** occurs at 0.80 V compared with 1.2 V for unsubstituted tetracylone under identical conditions (given in the caption of Figure 1). The electronic absorption spectra of **1** and unsubstituted tetracyclone are shown in Figure 2. Tetracyclone exhibits two characteristic absorptions at 508 and 336 nm with substitution in the 2,5 positions affecting the 508 nm absorbance and substitution in the 3,4 positions affecting the 336 nm absorbance.[19] Com-

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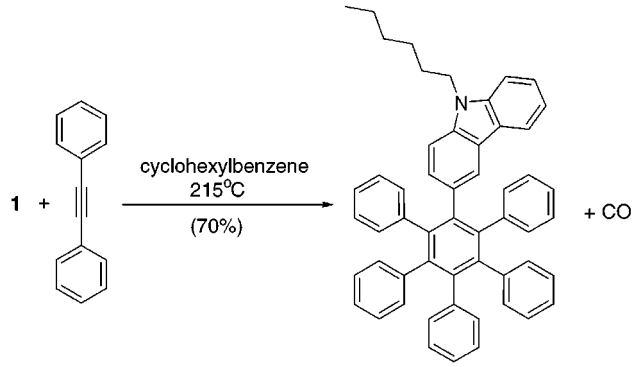
Scheme 2



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pound **1** shows a bathochromic shift with respect to tetracyclone (336 nm to 411 nm), similar to the *N*,*N*-dimethylaminobenzene-substituted tetracyclones.[19] These findings suggest there is extensive electronic interaction between the electron-rich carbazole ring and the cyclopentadieneone ring and that **1** is an activated diene for Diels−Alder-type cycloaddition reactions.

To test this conclusion, **1** was reacted with diphenylacetylene in a sealed tube at 215 °C for 8 h to give 1-[3-(9-hexyl)carbazoyl]-2,3,4,5,6-pentaphenylbenzene, **6**, in 70% yield (Scheme 2).

In conclusion, an improved two-step synthesis of unsymmetrical, heteroaromatic 1,2-diketones is reported. This procedure was used to synthesize a new class of carbazole-substituted tetracyclones that can act as dienes to produce polyaromatic compounds containing the carbazole moiety. Future work will include the synthesis of tetracyclones multisubstituted with carbazole and their use as dienes to produce polyaromatic macromolecules of interest in NLO and light-emitting applications.

Experimental Section

General Methods. All melting points recorded are uncorrected. Carbazole, brominated pyridines and thiophenes, phenylacetylene, CuI, 1,3-diphenylacetone, benzyltrimethylammonium hydroxide, and potassium permanganate were purchased from Aldrich Chemical Co. and used as received. $Pd(PPh_3)_4$[20] and 3-iodocarbazole[14] were synthesized according to published procedures. Toluene, dimethyl sulfoxide, diisopropylamine, and acetonitrile were distilled from CaH_2, under an argon atmosphere, prior to use and stored over 4 Å molecular sieves. Reagent-grade acetone was used as received from Fisher Chemical Co.

Electrochemical experiments were performed in a standard, single compartment three-electrode assembly using $Ag/AgNO_3$ in acetonitrile (0.1 M) as reference couple.

9-Hexyl-3-iodocarbazole (3). This procedure is a modification of the procedure given by Turner.[21] In a 500 mL flask immersed in a water bath and fitted with mechanical stirrer was added 100 mL of dimethyl sulfoxide followed by 18 g (0.302 mol) of finely powdered potassium hydroxide. To the rapidly stirred suspension was added dropwise a solution of 16 g (0.0546 mol) of 3-iodocarbazole in 25 mL of dimethyl sulfoxide. The color of the solution became dark brown during addition. The mixture was stirred at room temperature for 30 min, and 9.915 g (0.060 mol) of 1-bromohexane was added dropwise. The reaction was stirred for an additional 1 h and poured over ice−water. The solid precipitate was collected by filtration and washed thoroughly with water. Occasionally, the precipitate would not form, and the liquids were removed in vacuo. Recrystallization from hexane afforded 18.5 g (90%) of **3** as an off-white solid, mp 58−60 °C (lit.[13] mp 38 °C).

1-[3-(9-Hexyl)carbazoyl]-2-phenylethyne (4). In an oven-dried, 100 mL flask held under argon pressure was placed 3.000 g (7.95 mmol) of **3**, 25 mL of dry diisopropylamine, 15 mL of dry toluene, and 0.2758 g (3 mol %) of $Pd(PPh_3)_4$. The reaction mixture was heated to 60 °C, and 0.8118 g (7.95 mmol) of phenylacetylene and 0.0303 g (2 mol %) of CuI were added. The reaction was stirred under argon at 60 °C for 12 h. The flask was allowed to cool to room temperature, and 25 mL of diethyl ether was added. The mixture was washed with 10% HCl, water, and saturated aqueous NaCl and dried over Na_2SO_4. The solvent was evaporated, and the residue was chromatographed over silica gel using 20% ethyl acetate in hexane. The combined pure fractions yielded upon removal of the solvent 2.73 g (98%) of a yellow solid that was recrystallized from hexane and gave **4** as yellow needles: mp 82−83 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.33 (s, 1H), 8.12 (d, J = 7.5 Hz, 1H), 7.68−7.25 (m, 10H), 4.32 (t, J = 6.3 Hz, 2H), 1.95−1.82 (m, 2H), 1.48−1.25 (m, 6H), 0.89 (t, J = 5.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 140.7, 140.0, 131.4, 129.2, 128.3, 127.7, 126.0, 123.9, 122.8, 122.4, 120.5, 119.3, 113.0, 108.9, 108.7, 90.9, 87.5, 43.1, 31.5, 28.9, 26.9, 22.5, 14.0; FTIR (neat, cm^{-1}) 2212; HRMS (EI, *m*/*e*) calcd for $C_{26}H_{25}N$ 351.1987 (M^+), found 351.1998. Anal. Calcd for $C_{26}H_{25}N$: C, 88.85; H, 7.17; N, 3.98. Found: C, 89.11; H, 7.15; N, 3.84.

1-[3-(9-Hexyl)carbazoyl]-2-phenylethane-1,2-dione (5). The method of Srinivasan[11] was followed. The crude solid was chromatographed over silica with 10% ethyl acetate in hexane as eluent. The combined pure fractions yielded upon removal of the solvent 2.11 g (96%) of a yellow solid that was recrystallized from a 3:1 ether−hexane solution and gave **5** as yellow needles: mp 93−94 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.73 (s, 1H), 8.18−8.04 (m, 3H), 7.70−7.64 (m, 1H), 7.58−7.44 (m, 5H), 7.35−7.26 (m, 2H), 4.35 (t, J = 8.2 Hz, 2H), 1.98−1.82 (m, 2H), 1.49−1.2 (m, 6H), 0.88 (m, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 195.5, 194.2, 144.2, 141.3, 134.6, 133.5, 130.0, 128.9, 127.5, 126.8, 123.9, 122.9, 120.9, 120.5, 109.4, 108.9, 43.4, 31.5, 28.8, 26.8, 22.5, 13.9; FTIR (neat, cm^{-1}) 1675, 1656; HRMS (EI, *m*/*e*) calcd for $C_{26}H_{25}NO_2$ (M^+) 383.1885, found 383.1898. Anal. Calcd for $C_{26}H_{25}NO_2$: C, 81.43; H, 6.57; N, 3.65. Found: C, 81.49; H, 6.29; N, 3.52.

3-[3-(9-Hexyl)carbazoyl]-2,4,5-triphenylcyclopenta-2,5-dien-1-one (1). In a 5 mL reaction vessel were placed 0.3546 g (0.926 mmol) of **5**, 0.1948 g (0.926 mmol) of 1,3-diphenylacetone, and 1.5 mL of triethylene glycol. The mixture was heated to 100 °C, and 0.142 mL of a 40 wt % solution in MeOH of benzyltrimethylammonium hydroxide was carefully added in one portion under the surface of the reaction. The dark brown mixture was stirred at 100 °C for 10 min and poured into ice−water. The mixture was extracted with methylene chloride. The combined extracts were washed with saturated aqueous NaCl and dried over Na_2SO_4. Removal of the solvent gave a brown oil that was chromatographed over silica gel with 1:1 methylene chloride−hexane as eluent. The pure fractions yielded 0.3760 g (73%) of a brown solid that was recrystallized from acetonitrile and gave **1** as brown needles: mp 176−177 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, J = 6.9 Hz, 1H), 7.55 (s, 1H), 7.47−6.96 (m, 20H), 4.23 (t, J = 8.0 Hz, 2H), 1.93−1.78 (m, 2H) 1.45−1.22 (m, 6H), 0.88 (t, J = 5.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 200.5, 155.7, 154.4, 140.5, 133.5, 131.4, 130.9, 130.2, 129.5, 128.3, 127.9, 127.6, 127.3, 127.0, 125.9, 124.0, 123.1, 122.7, 122.0, 120.2, 119.2, 108.8, 108.1, 43.2, 31.5, 28.9, 26.9, 22.5, 13.9. FTIR (neat, cm^{-1}) 1703; HRMS (EI, *m*/*e*) calcd for $C_{41}H_{35}NO$ (M^+) 557.2719, found 557.2741. Anal. Calcd for $C_{41}H_{35}NO$: C, 88.30; H, 6.32; N, 2.51. Found: C, 87.94; H, 6.22; N, 2.41.

1-[3-(9-Hexyl)carbazoyl]-2,3,4,5,6-pentaphenylbenzene (6). To a 10 mL glass ampule was added 0.1000 g (0.179 mmol) of **1**, 0.0319 g (0.179 mmol) of diphenylacetylene, and 3 drops of cyclohexylbenzene. The glass ampule was deoxygenated by three freeze−pump−thaw cycles and evacuated to 0.01 mmHg. The ampule was sealed under vacuum by way of a torch and heated to 215 °C for 8 h. The ampule was allowed to cool to room temperature and carefully opened (*caution: contents may be under pressure*), and the solids were dissolved in $CHCl_3$ and chromatographed over silica gel using 30% $CHCl_3$ in hexane as eluent. The pure fractions yielded upon removal of the solvent 0.0887 g (70%) of an off-white solid that was recrystallized from

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(21) Turner, S. R.; Pai, D. M. *Macromolecules* **1979**, *12*, 1.

methylcyclohexane and gave **6** as a white powder: mp 245−246 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.78 (d, J = 7.5 Hz, 1H), 7.57−7.53 (m, 1H), 7.39−7.29 (m, 1H), 7.12−7.06 (m, 1H), 7.05−6.65 (m, 28H), 4.10 (t, J = 7.0 Hz, 2H), 1.81−1.65 (m, 2H), 1.35−1.17 (m, 6H), 0.9−0.78 (m, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 140.8, 140.2, 138.4, 131.4, 129.4, 126.5, 125.0, 123.5, 123.0, 121.4, 119.9, 118.2, 108.4, 106.7, 42.8, 31.5, 28.7, 26.7, 22.5, 13.9; HRMS (FAB, m/z) calcd for $C_{54}H_{45}N$ (M^+) 707.3552, found 707.3551. Anal. Calcd for $C_{54}H_{45}N$: C, 91.61; H, 6.41; N, 1.98. Found: C, 91.47; H, 6.29; N, 1.88.

Acknowledgment. This work is supported in part by the U.S. Army Research Office under Grant No. DAAH04-96-I-0130 and by the IIT-ERIF grant.

JO9904213