

Synthesis of Derivatives of Phenanthrene and Helicene by Improved Procedures of Photocyclization of Stilbenes

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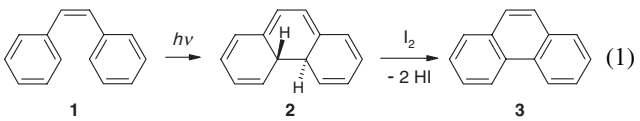
An improved method has been developed for photocyclization of stilbene to construct phenanthrenes and benzo[*c*]phenanthrenes. This reaction is promoted by iodine while tetrahydrofuran is used as an efficient and inexpensive scavenger of hydroiodic acid produced during the photocyclization sequence. In another process, cyclohexene is used as a reagent for dehydrogenation step in place of THF–I_2.

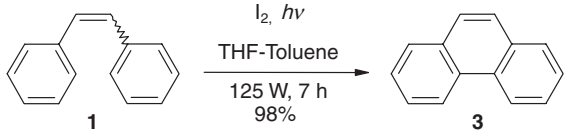
A common method for synthesis of phenanthrene involves the construction of a central ring by photocyclization of stilbene.[1] This method involves exposure of *cis*-/*trans*-stilbene to UV light, which causes its isomerization to cis form **1**, which undergoes electrocyclic ring formation to produce dihydrophenanthrene **2**. This intermediate **2** undergoes oxidation in the presence of iodine to generate the aromatic ring of **3** and HI, eq 1. This method is used extensively for the preparation of a large number of polycyclic aromatic compounds,[2] helicenes,[3] aza-helicenes,[4] thia-helicenes,[5] complex heterocyclic compounds,[6] and molecular devices.[7]



(1)

The oxidative conversion of **2** to **3** is accompanied by reduction of iodine to produce two moles of hydrogen iodide. The photolysis is usually carried out in the presence of excess of propylene oxide or ethylene oxide. The strong acid by-product, HI, is thus neutralized in the opening of the epoxide ring of these reagents. Alternatively, the photocyclization can be carried out in the presence of oxygen[8] with good results. It is reported that when a primary amine is used as the scavenger of this HI, the cyclization favors an ionic mechanism and gives dihydro derivative.[9] Other bases have been used as acid scavengers in this type of photocyclization with some success.[4b,10] An analogous reaction of photochemical cyclization of stilbazole salts within a Nafion membrane micro-reactor has been reported,[11] without using any base nor iodine.

In this article we present the use of tetrahydrofuran as a neutral, easily available, inexpensive scavenger of hydroiodic acid produced in this type of photocyclization. The acid promoted opening of tetrahydrofuran when exposed to in situ generated HI should give 4-iodobutan-1-ol or 1,4-diiodobutane.[12] To test this concept a sample of mainly *trans*-stilbene was exposed to light from a 125-W high pressure mercury vapor lamp (hpmv) in a routine immersion well photoreactor with iodine (1.1 equiv), tetrahydrofuran (20 equiv) in toluene for 7 h, eq 2. The product formed was separated and identified as phenanthrene (TLC, mp, and NMR). The isolated yield of **3** was excellent and much higher than reportedly obtained with propylene oxide or with oxygen.[1c,3h] To the best of our knowledge THF has not been used as HI scavenger in such cases, although occasionally used as a solvent. However, there is a literature reference[13] of the combined use of excess of THF and propylene oxide, where HI should preferentially react with the more strained epoxide ring than the former. This means that the THF is actually used only as solvent and may not work as scavenger of HI in this reported case.[13]



(2)

There is the possibility of the oxygen from air to act as oxidant in place of I_2 as known from the literature. To test this, another experiment was run with careful degassing the reaction mixture by applying vacuum and sonication and subjected to photoirradiation. However, the same result was obtained confirming that I_2–THF is the actual reagent for the second step. A separate experiment with I_2–toluene but without THF was very sluggish, establishing the role of THF.

Encouraged by this result a number of stilbene derivatives were synthesized by Wittig reaction[3k] and subjected to the photocyclization under the present, modified conditions, Table 1. A series of mono- and di-substituted phenanthrenes were obtained after careful chromatography and showed satisfactory ^{1}H NMR analysis. It is noteworthy to have succeeded in photocyclization of nitro-substituted stilbene to the corresponding phenanthrene, which was known to be difficult.[1d,1f]

As a part of our ongoing research project we are required to develop an expeditious synthesis of functionalized benzo[*c*]-phenanthrene or helicenes. With this aim several β-styrylnaphthalenes were prepared by Wittig reaction[3k] and subjected to the current photocyclization, Table 2. A mixture of cis and trans isomer was used for the reaction and its ratio had not much influence on the efficacy of the cyclization.

Another derivative of stilbene **15** was prepared and subjected to this photocyclization. The cyclization reaction can take place

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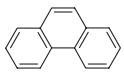
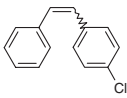
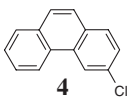
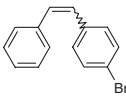
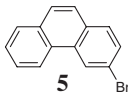
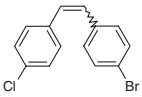
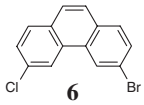
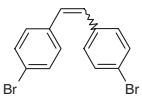
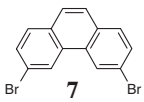
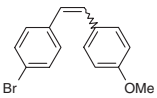
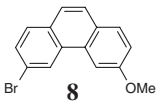
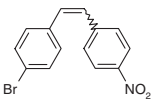
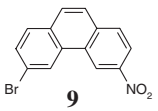
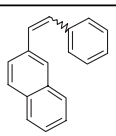
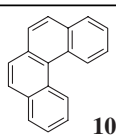
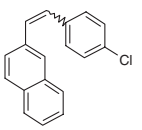
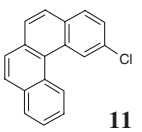
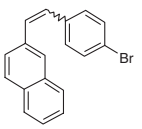
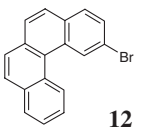
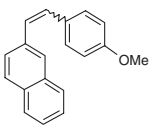
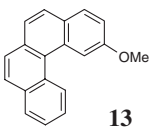
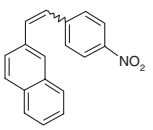
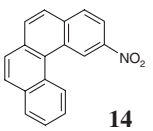
Table 1. Photocyclization of Stilbenes with I_2–THF

Entry	Stilbene	Phenanthrene	Time/h with 125-W hpmv lamp	Isolated yield/% [Reported yield/%]	Mp/°C (Lit)
1		 **3**	7	98 [73][a)]	100–01 (98–100)
2		 **4**	7	78 [76][a)]	79–81 (79–80)[a)]
3		 **5**	20	84 [76][a)]	80–82 (81–83)[a)]
4		 **6**	9	83	186–188
5		 **7**	16	97 [77][b)]	194 (194)[c)]
6		 **8**	40	47	100–102
7		 **9**	29	68	234–235

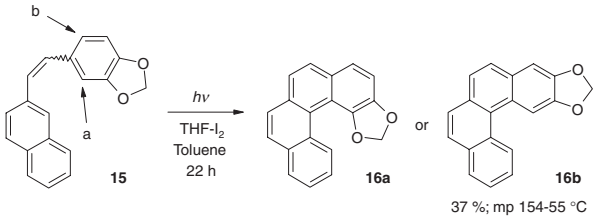
a) Ref. 1d. b) Ref. 2c. c) Ref. 1e.

Table 2. Photocyclization of β-Styrylnaphthalenes with I_2–THF

Entry	Stilbene	Benzo[*c*]phenanthrene	Time/h with 125-W hpmv lamp	Isolated yield/% [Reported yield/%]	Mp/°C (Lit)
1		 **10**	13	84	68–69 (67–68)[b)]
2		 **11**	16	67	62–64
3		 **12**	20	96 [78][a)]	87–88 (87–88)[c)]
4		 **13**	22	75	78–80 (78–79)[b)]
5		 **14**	23	83	150–152

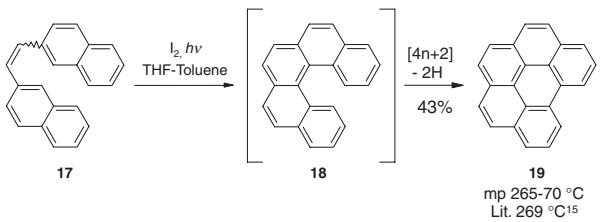
a) Ref. 2d. b) Ref. 14a. c) Ref. 14b.

at two sites, at "a" or at "b" (eq 3), leading to formation of **16a** or **16b** respectively. The cyclization in the present conditions resulted in the isolation of linear product **16b**, established by its ^{1}H NMR. Probably the desired cyclization at "a" site is difficult due to steric constraints.



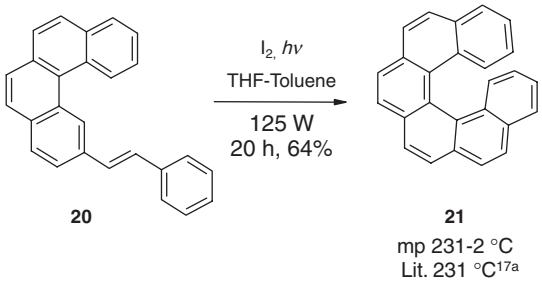
(3)

Optically pure [5]helicenes was recently used as chiral source in asymmetric addition of dialkyl zinc to aldehydes.[15] This helicenes can be prepared by photolysis of dinaphthylethene **17** under the present conditions. However, under the standard conditions of prolonged irradiation, the initially formed [5]helicene (**18**), was further converted to benzo[*ghi*]perylene (**19**), eq 4. This observation of $[4n + 2]$ electrocyclic ring closure has been previously documented in the literature.[16]



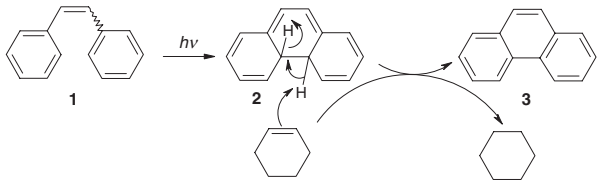
(4)

However, under similar conditions it was possible to synthesize [6]helicene (**21**) from **20** in moderate yield. The isolated **21** shows identical melting point[17a] and NMR to one reported recently,[17c] eq 5.



(5)

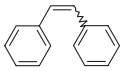
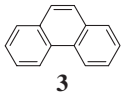
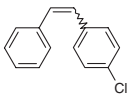
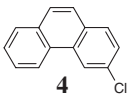
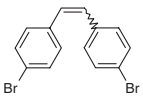
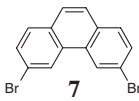
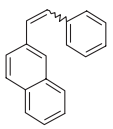
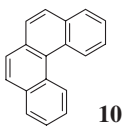
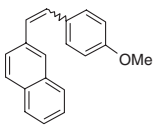
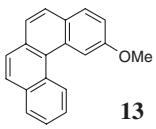
The first step of this photocyclization is the formation of **2** and our present modification deals with the second step, i.e., aromatization toward **3**. In this part of the conversion we have envisaged the use of cyclohexene to abstract the hydrogen as shown in eq 6. To test this concept a sample of *trans*-stilbene was exposed to photolysis in the presence of excess of cyclohexene (20 equiv) in toluene.



(6)

A careful isolation of the product indicated the formation of phenanthrene in good yield and we have extended this preliminary work to a few more examples, Table 3. Further work in this method is currently underway.

Table 3. Photocyclization of Stilbene and β-Styrylnaphthalenes in the Presence of Cyclohexene

Entry	Stilbene	Benzo[*c*]-phenanthrene	Time/h with 125-W hpmv lamp	Isolated yield/%
1		 **3**	16	86
2		 **4**	23	63
3		 **7**	20	54
4		 **10**	17	36
5		 **13**	18	35

In summary, we have developed two simple and efficient methods for photocyclization of substituted stilbenes to phenanthrenes and benzo[*c*]phenanthrenes using readily available and cheap chemicals. In the first one the boiling point of THF is sufficiently high compared to propylene oxide (bp 34 °C) and hence it is convenient to use it in a routine photoreactor, which gets slightly warm even with water circulation. In the second method we report novel use of cyclohexene to assist the second part of the cyclization sequence. The low cost and easy availability of the reagents are the main advantages of these methods.

Experimental

Preparation of Phenanthrene. Method-1: A solution of *trans*-stilbene (0.1 g, 0.55 mmol) and iodine (0.154 g, 0.61 mmol) in toluene (425 mL) and tetrahydrofuran (0.9 mL, 11.09 mmol, ca. 20 mol equivalent) was irradiated in a standard immersion well photoreactor with 125-W high pressure mercury vapor lamp for 7 h or until no starting olefin was seen by TLC. The reaction mixture was then washed with aqueous sodium thiosulfate, water, brine and dried over anhydrous sodium sulfate. The concentrated mixture was purified on silica gel column to afford phenanthrene as white solid (0.097 g, 98%).

Method-2: A solution of *trans*-stilbene (0.1 g, 0.55 mmol) and cyclohexene (0.91 g, 1.1 mmol) in toluene (425 mL) was irradiated in a standard immersion well photoreactor with a 125-W high pressure mercury vapor lamp for 16 h. The reaction mixture was dried on anhydrous sodium sulfate, concentrated at reduced pressure and purified on silica gel column to get phenanthrene as white solid (0.086 g, 86%).

The molecules listed in Table 1, Table 2 were prepared by Method-1 and in Table 3 by Method-2.

Spectral Data of Selected Molecules. 3-Bromo-6-chlorophenanthrene (6): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.58 (dd, $J = 8.5$, 2.1 Hz, 1H), 7.67–7.73 (m, 3H), 7.75–7.77 (d, $J = 8.5$ Hz, 1H), 7.81–7.83 (d, $J = 8.5$ Hz, 1H), 8.54 (d, $J = 1.96$ Hz, 1H), 8.71 (d, $J = 1.64$ Hz, 1H). IR (KBr): ν 3051, 2923, 1588, 1497, 1429, 1409, 1109, 1088, 1074, 1021, 836, 771, 740, 696, 587, 520 cm^{-1}.

3-Bromo-6-methoxyphenanthrene (8): ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.03 (s, 3H), 7.54–7.56 (d, $J = 8.8$ Hz, 1H), 7.65–7.74 (m, 3H), 7.72–7.74 (d, $J = 9.2$ Hz, 1H), 7.78–7.81 (d, $J = 8.8$ Hz, 1H), 7.91 (d, $J = 2.4$ Hz, 1H), 8.71 (d, $J = 1.5$ Hz, 1H). IR (KBr): ν 3011, 2962, 2931, 1615, 1590, 1510, 1460, 1444, 1255, 1220, 1073, 1028, 866, 843, 777, 592, 553, 537 cm^{-1}.

3-Bromo-6-nitrophenanthrene (9): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.83 (m, 2H), 7.82–7.84 (d, $J = 8.8$ Hz, 1H), 7.90–7.92 (d, $J = 8.8$ Hz, 1H), 8.02–8.04 (d, $J = 8.8$ Hz, 1H), 8.41–8.44 (dd, $J = 8.8$, 2.2 Hz, 1H), 8.89 (d, $J = 2.2$ Hz, 1H), 9.52 (d, $J = 2.4$ Hz, 1H). IR (KBr): ν 3082, 2925, 1621, 1591, 1530, 1497, 1437, 1342, 1075, 1028, 845, 736, 588, 509 cm^{-1}.

2-Chlorobenzo[*c*]phenanthrene (11): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.58 (dd, $J = 8.6$, 2.0 Hz, 1H), 7.63–7.66 (m, 1H), 7.71–7.75 (m, 1H), 7.80–7.87 (m, 3H), 7.90–7.93 (d, $J = 8.5$ Hz, 1H), 7.93–7.95 (d, $J = 8.5$ Hz, 1H), 8.01–8.03 (dd, $J = 7.7$, 0.8 Hz, 1H), 9.03–9.06 (d, $J = 9.7$ Hz, 1H), 9.11 (d, $J = 1.3$ Hz, 1H). IR (KBr): ν 3046, 2924, 1596, 1487, 1440, 1419, 1110, 1092, 1039, 838, 779, 747 cm^{-1}.

2-Bromobenzo[*c*]phenanthrene (12): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.65 (d, $J = 7.3$ Hz, 1H), 7.65–7.67 (d, $J = 7.4$ Hz, 1H), 7.71–7.74 (d, $J = 8.4$ Hz, 1H), 7.74–7.76 (d, $J = 7.2$ Hz, 1H), 7.80–7.82 (d, $J = 8.4$ Hz, 1H), 7.82–7.85 (d, $J = 8.5$ Hz, 1H), 7.87–7.90 (d, $J = 8.6$ Hz, 1H), 7.91–7.93 (d, $J = 8.6$ Hz, 1H), 8.02–8.04 (d, $J = 7.9$ Hz, 1H), 9.03–9.05 (d, $J = 8.5$ Hz, 1H), 9.48 (s, 1H). IR (KBr): ν 3044, 1600, 1588, 1485, 1440, 1109, 1082, 1039, 839, 781, 746, 599, 570, 529 cm^{-1}.

2-Methoxybenzo[*c*]phenanthrene (13): ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.01 (s, 3H), 7.27–7.30 (dd, $J = 8.8$, 2.5 Hz, 1H), 7.59–7.62 (m, 1H), 7.64–7.68 (m, 1H), 7.68–7.70 (d, $J = 8.4$ Hz, 1H), 7.79–7.88 (m, 3H), 7.92–7.94 (d, $J = 7.9$ Hz, 1H), 8.01 (dd, $J = 7.8$, 1.4 Hz, 1H), 8.58–8.59 (d, $J = 2.4$ Hz, 1H), 9.18–9.20 (d, $J = 8.5$ Hz, 1H). IR (KBr): ν 3001, 2951, 2925, 1608, 1505, 1449, 1239, 1219, 1102, 1045, 881, 836, 749 cm^{-1}.

2-Nitrobenzo[*c*]phenanthrene (14): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.72 (m, 1H), 7.77–7.81 (m, 1H), 7.81–7.84 (d, $J = 8.5$ Hz, 1H), 7.91–7.93 (d, $J = 8.5$ Hz, 1H), 7.96–7.98 (d, $J = 7.8$ Hz, 1H), 7.98–8.00 (d, $J = 8.5$ Hz, 1H), 8.04–8.06 (dd, $J = 8.7$, 2.4 Hz, 1H), 8.06–8.09 (d, $J = 8.9$ Hz, 1H), 8.35–8.38 (dd, $J = 8.8$, 2.2 Hz, 1H), 8.95–8.97 (d, $J = 8.5$ Hz, 1H), 9.99–10.0 (d, $J = 2.0$ Hz, 1H). IR (KBr): ν 3052, 3006, 2924, 1601, 1530, 1510, 1378, 1334, 845, 828, 800, 759, 736 cm^{-1}.

Benzo[*c*]phenanthreno[2,3-*d*]-1,3-dioxole (16b): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13 (s, 2H), 7.33 (s, 1H), 7.58–7.66 (two overlapping m, 2H), 7.69–7.82 (four overlapping d, 4H), 7.97–7.99 (dd, $J = 7.8$, 1.5 Hz, 1H), 8.51 (s, 1H), 9.01–9.04 (d, $J = 8.4$ Hz, 1H). IR (KBr): ν 3049, 2905, 1602, 1494, 1463, 1200, 1172, 1119, 1071, 1036, 857, 833, 796, 761 cm^{-1}

Benzo[*ghi*]perylene (19): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97–8.05 (d, $J = 7.8$ Hz, 2H), 8.05–8.09 (d, $J = 8.8$ Hz, 2H), 8.11–8.15 (d, $J = 8.9$ Hz, 2H), 8.16–8.21 (dd, $J = 7.7$, 0.8 Hz, 2H), 8.34 (s, 2H), 8.98–9.02 (dd, $J = 7.8$, 0.8 Hz, 2H).

[6]Helicene (21): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65–6.69 (ddd, $J = 8.2$, 1.0, 1.0 Hz, 2H), 7.19–7.23 (dd, $J = 7.7$, 7.2 Hz, 2H), 7.57–7.59 (d, $J = 8.6$ Hz, 2H), 7.83–7.88 (d, $J = 8.0$ Hz, 2H), 7.90–7.95 (m, 4H), 7.96–8.01 (m, 4H). IR (KBr): ν 3042, 1601, 1500, 1468, 1434, 844, 828, 799, 753 cm^{-1}.

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