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Notes

Palladium-Catalyzed Annulation Reactions of 1,8-Diiodonaphthalene[†,1]

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Introduction

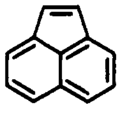
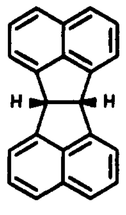
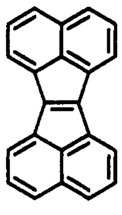
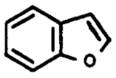
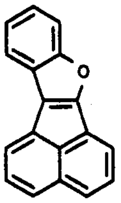
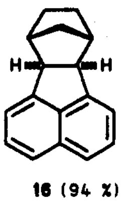
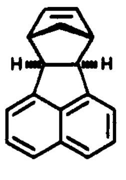
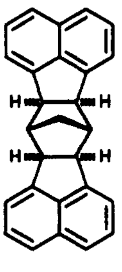
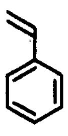
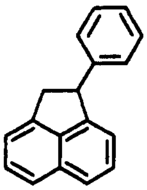
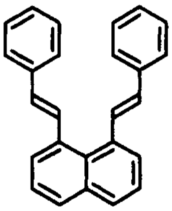
Transition metal catalyzed processes have been proven to be extremely useful for the synthesis of annulated ring systems.[2] Nevertheless their application to the synthesis of polycyclic aromatic hydrocarbons has been clearly underutilized.[3] Recently, we reported a palladium-catalyzed annulation reaction of 1,8-diiodonaphthalene (1) and acenaphthylene (2), gaining straightforward access to acenaphth[1,2-*a*]acenaphthylene (8), a strained hexacyclic compound difficult to obtain by other reported methods.[4] This paper presents in detail our studies on scope and limitations of palladium-catalyzed annulation reactions with 1,8-diiodonaphthalene (1) for the synthesis of acenaphthylene derivatives.

Results and Discussion

In our preliminary communication[5] we reported that the annulation reaction of 1,8-diiodonaphthalene (1) and acenaphthylene (2) is performed by a catalytic system generated in situ from $Pd(OAc)_2$, DMF, K_2CO_3, and n-Bu_4NBr (100 °C, 24 h). By this method acenaphth[1,2-*a*]acenaphthylene (8) is obtained in a single preparative step with 42% yield (Table I, entry 1). This reaction is only slightly water sensitive; the addition of 3 equiv of water hardly influences the yield of 8 (36%). Whereas the presence of a base, for instance K_2CO_3, is indeed necessary for the reaction to occur, the presence of an ammonium salt is not (Table II). Without a phase-transfer catalyst 8 is still obtained in 29% yield. Tetraalkylammonium bromides do increase the yield, n-Bu_4NI does not seem to have an influence, and ammonium chlorides inhibit the reaction. The system bis(triphenylphosphine)-palladium dichloride/sodium acetate in DMF also gives satisfying results (37% yield).

The formation of the dihydro derivative 5 as a byproduct with 6% isolated yield (Table I, entry 1) is rather unusual; formaly iodine has been eliminated and not hydrogen iodide as in a normal Heck reaction.[6] Therefore some mechanistic features of this annulation process should be discussed (Scheme I). Presumably an aryl–palladium iodide complex formed by oxidative addition of a Pd(0) species to the aryl iodide 1 adds to acenaphthylene (2) in a syn manner[6] to generate the key intermediate 4. The elimination of palladium iodide under C–C bond formation giving rise to 5 is not yet fully understood. Pd(IV) intermediates that have been discussed in detail very recently[7] might be involved. According to our own

Table I. Annulation Reactions of 1 with Alkenes

entry	alkenes (equiv, reactn time)	products (yield)[a]
1	 2 (2 equiv., 1 d)	 5 (6 %)  8 (42 %)
2	 13 (10 equiv., 3 d)	 14 (10 %)
3	 15 (5 equiv., 3 d)	 16 (94 %)
4	 17 (2 equiv., 3 d)	 18 (37 %)  19 (17 %)
5	 20 (10 equiv., 3 d)	 21 (17 %)  22 (17 %)

[a] Isolated yields of purified compounds are given; yields are not optimized except for entry 1; conditions: 5 mol % $Pd(OAc)_2$, K_2CO_3, n-Bu_4NBr, DMF, N_2, 100 °C.

[†] Dedicated to Professor Richard P. Kreher on the occasion of his 60th birthday.

(1) Transition Metal Catalyzed Annulation Reactions; Part 3. Part 2: Dyker, G. *Angew. Chem., Int. Ed. Engl.*, in press.

(2) Trost, B. M. *Science* 1991, *254*, 1471.

(3) Rice, J. E.; Cai, Z.-W. *Tetrahedron Lett.* 1992, *33*, 1675.

(4) Mitchell, R. H.; Fyles, T.; Ralph, L. M. *Can. J. Chem.* 1977, *55*, 1480.

(5) Dyker, G. *Tetrahedron Lett.* 1991, *32*, 7241.

(6) (a) Heck, R. F. *Org. React.* 1982, *27*, 345. (b) Heck, R. F. *Acc. Chem. Res.* 1979, *12*, 146.

(7) Canty, A. J. *Acc. Chem. Res.* 1992, *25*, 83.

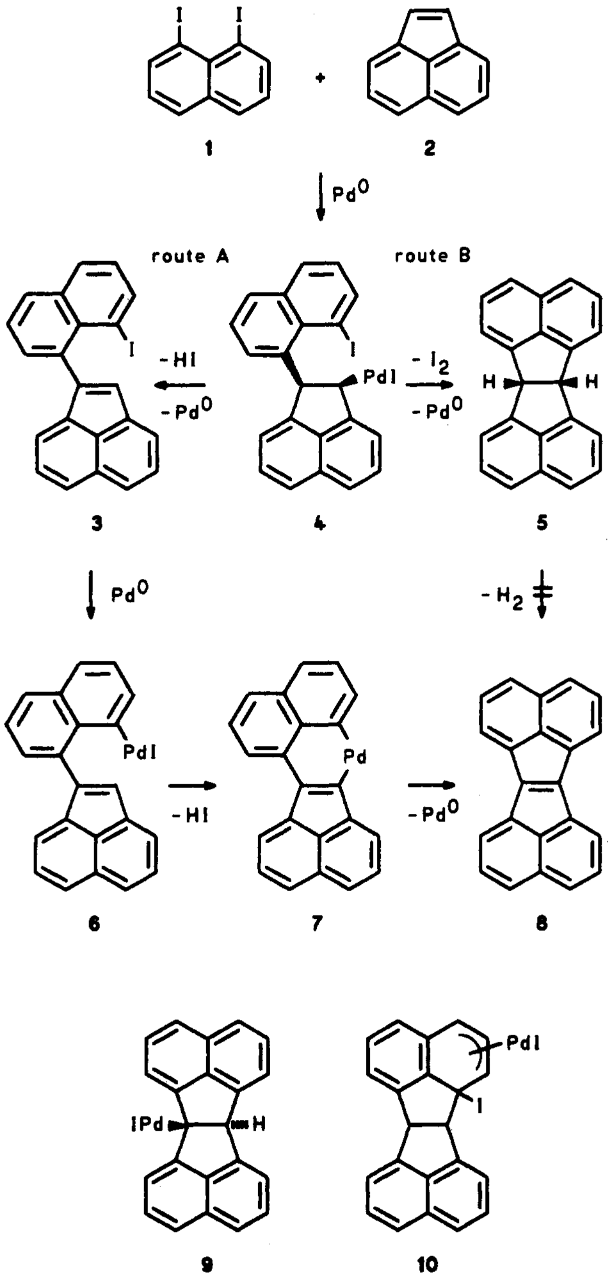
0022-3263/93/1958-0234$04.00/0

Table II. Influence of Tetraalkylammonium Salts on the Formation of Hydrocarbon 8

entry	ammonium salt	yield of 8 (%)[a]
1	*n*-Bu_4NBr	42
2	*n*-Oct_4NBr	40
3	none	29
4	*n*-Bu_4NI	25
5	*n*-Bu_4NCl	3
6	$BzEt_3NCl$	3

[a] Isolated yields are given; conditions: 1 (1 mmol), 2 (2 mmol), $Pd(OAc)_2$ (5 mol %), ammonium salt (2 mmol), K_2CO_3 (8 mmol), DMF (10 mL), N_2, 100 °C, 3 d.

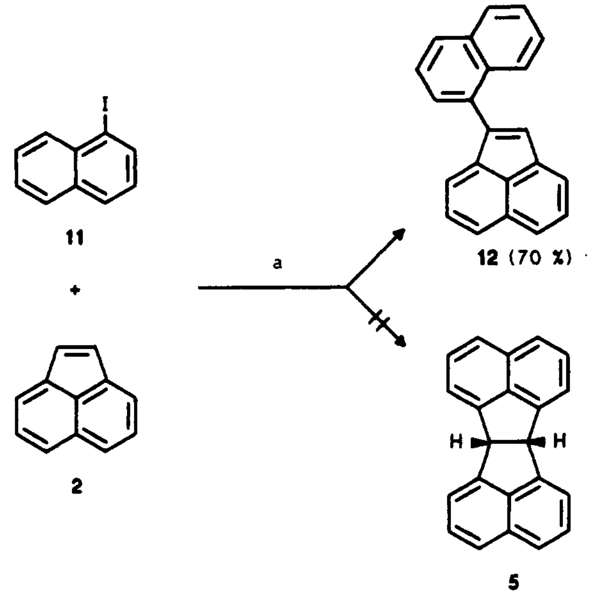
Scheme I



observations iodide is consumed under the reaction conditions either by disproportionation or reduction. 5 itself is stable in the presence of the catalyst; hydrogen elimination to 8 does not occur. Thus 5 is a true byproduct and not an intermediate.

Since the β-hydrogen and the Pd substituent of 4 exhibit a trans configuration, the elimination to 3 might be hindered.[6] Nevertheless a few analogous examples of a *trans*-β-hydride elimination as an overall process are known, generally with the palladium in a benzylic position.[8] Therefore this process is probably proceeding through radical or ionic intermediates. Although 3 could not be identified in the reaction mixture, its occurance is feasible. In analogy 12 is formed by the Heck reaction of 2 and 11 rather nicely (Scheme II); in this case the expected formation of 5 is not observed. Presumably 3 is transformed to 8 via an intramolecular dehydrohalogenation with 6 and 7 as intermediates. The trans-fused complex 9, generated by an intramolecular syn addition, is less likely because of its enormous ring strain. The π-allyl–Pd complex 10 directly formed from 4 cannot be completely ruled out as an intermediate. Similar complexes have been shown to occur in palladium induced carbocyclization reactions of aryl rings.[9]

Scheme II[a]



[a] (a) 5 mol % $Pd(OAc)_2$, K_2CO_3, *n*-Bu_4NBr, DMF, N_2, 100 °C, 3 d.

To determine scope and limitations of this annulation reaction a variety of alkenes have been tested (Table I). The formation of the completely unsaturated product like in entry 2 with benzo[*b*]furan (13) obviously is the exception; the annulation under deiodination in analogy to route B (Scheme I) is more frequently observed. Only with especially reactive olefins like norbornene (15) and norbornadiene (17) are good yields obtained (up to 94%, entry 3). With styrene (20) as the alkene component a complex product mixture is formed, containing the 1:1 annulation product 21, the 1:2 product 22 and apparently several noncharacterized 2:2 products. Alkenes such as phenanthrene, *cis*- and *trans*-stilbene, 1,1-diphenylethene, cyclohexene, cyclohexenone, naphthoquinone, and 3,4-dihydro-2*H*-pyran did not react at all. In these cases Ullmann products[10] 23 and 24 of 1,8-diiodonaphthalene (1) were isolated (Table III). The binaphthyl derivative 23 can be cyclized in good yield to the final product perylene (24) by prolonged heating under the reaction conditions (Table III, entry 2). As a control experiment iodobenzene

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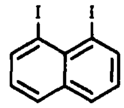
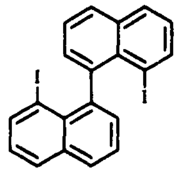
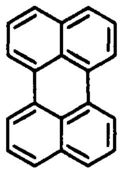
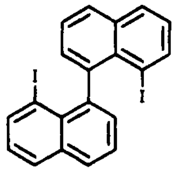
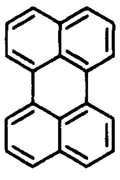
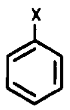
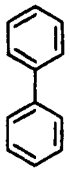
(8) (a) Horino, H.; Arai, M.; Inoue, N. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1683. (b) Dieck, H. A.; Heck, R. F. *J. Organomet. Chem.* **1975**, *93*, 259.

(9) (a) Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550. (b) Pfeffer, M.; Sutter, J.-P.; Rotteveel, M. A.; De Cian, A.; Fischer, J. *Tetrahedron* **1992**, *48*, 2427.

(10) Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 977.

Table III. Palladium-Catalyzed Ullmann Coupling Reactions

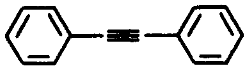
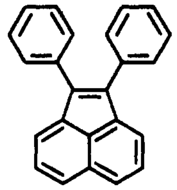
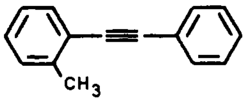
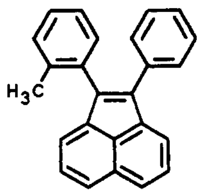
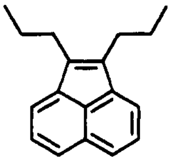
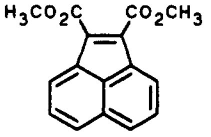
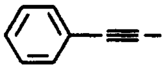
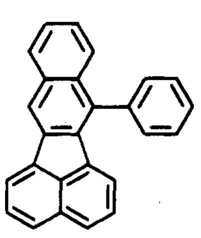
entry	aryl halide (reactn time)	products (yield)[a]	
1	 1 (3 d)	 23 (39 %)	 24 (42 %)
2	 23 (7 d)	 24 (85 %)	
3	 25a: X = I (3 d)	 26 (75 %)	
4	25b: X = Br (3 d)	(25 %)	
5	25c: X = Cl (3 d)		

[a] Isolated yields are given; conditions: 5 mol % $Pd(OAc)_2$, K_2CO_3, n-Bu_4NBr, DMF, N_2, 100 °C.

(**25a**) was coupled to biphenyl (**26**) in 75% yield. The coupling reaction is less efficient with bromobenzene (**25b**) and fails with chlorobenzene (**25c**). As a result these reaction conditions[11] for the palladium-catalyzed Ullmann coupling reaction seem to be equally efficient as the one reported by Grigg,[12] but in our case addition of the expensive and toxic hexabutylditin is not necessary. Probably the solvent DMF is directly functioning as a reducing agent or indirectly by its decomposition products carbon monoxide and dimethylamine.[13]

The successful deiodination leading to Ullmann coupling products prompted us to evaluate acetylene derivatives as annulation partners for 1,8-diiodonaphthalene (**1**). In general, substituted acenaphthylene derivatives are indeed obtained with moderate yields (Table IV). By using a large excess of the acetylenic component the yield is distinctly improved (entry 2). However, the Ullmann products **23** and **24** are still found as byproducts. The electron poor dicarboxylic acid ester **33** is significantly less reactive than diaryl- and dialkylalkynes. The reaction with phenylacetylene **35** is an exception. In this case the benzo[*k*]fluoranthene derivative **36** is isolated, known as a cyclization product of 1,8-bis(phenylethynyl)naphthalene.[14]

Table IV. Annulation Reactions of 1 with Alkynes

entry	alkynes (equiv)	products (yield)[a]
1	 27 (2 equiv.)	 28 (48 %)
2	(10 equiv.)	(72 %)
3	 29 (2 equiv.)	 30 (30 %)
4	 31 (2 equiv.)	 32 (47 %)[b]
5	$H_3CO_2C-\equiv-CO_2CH_3$ 33 (2 equiv.)	 34 (14 %)
6	 35 (2 equiv.)	 36 (41 %)

[a] Isolated yields are given; conditions: 5 mol % $Pd(OAc)_2$, K_2CO_3, n-Bu_4NBr, DMF, N_2, 100 °C, 3 d. [b] Contaminated with 13% of an isomer with exocyclic double bond.

In comparison to the reactivity of the diiodide **1**, iodobenzene **25a** was tested as the aryl halide component in the annulation reaction with substituted acetylenes (Scheme III). Most interestingly 2 equiv of **25a** are condensed with diphenylacetylene (**27**) giving rise to 9,10-diphenylphenanthrene (**37**) in good yield, a process similar to the annulation reaction of **25a** with norbornene studied by Chiusoli and de Meijere.[15] In contrast to our result Cacchi[16] and Heck[17] observed formation of triphenylethene and 1,2,3,4-tetraphenylnaphthalene, respectively, under slightly different reaction conditions. The regiochemistry and applications of this new method for the synthesis of substituted phenanthrenes is currently under investigation and should be extended to heterocyclic systems.

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[11] Similar reaction conditions for the palladium-catalyzed Ullmann coupling have been studied in detail by A. de Meijere and co-workers; private communication, M. Weber, Dissertation, Hamburg, 1992.

[12] Grigg, R.; Teasdale, A.; Sridharan, V. *Tetrahedron Lett.* **1991**, *32*, 3859.

[13] Kadish, K. M.; Araullo-McAdams, C.; Han, B. C.; Franzen, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 8364.

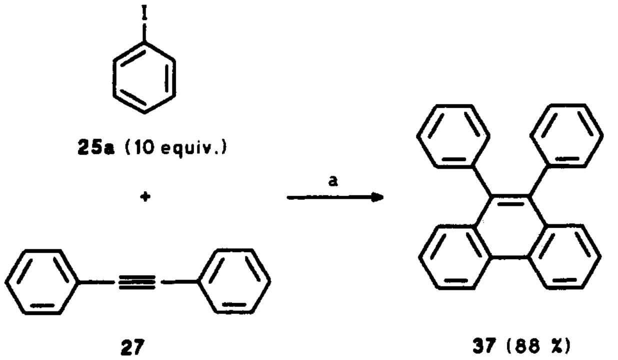
[14] Staab, H. A.; Ipaktschi, J. *Chem. Ber.* **1971**, *104*, 1170.

[15] (a) Catellani, M.; Chiusoli, G. P.; Costa, M. *Pure Appl. Chem.* **1990**, *62*, 623. (b) Reiser, O.; Weber, M.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1037.

[16] Cacchi, S.; Felici, M.; Pietroni, B. *Tetrahedron Lett.* **1984**, *25*, 3137.

[17] Wu, G.; Rheingold, A. L.; Geib, S. J.; Heck, R. F. *Organometallics* **1987**, *6*, 1941.

Scheme III[a]



[a] (a) 5 mol % $Pd(OAc)_2$, K_2CO_3, n-Bu_4NBr, DMF, N_2, 100 °C, 3 d.

In conclusion, palladium-catalyzed coupling reactions of 1,8-diiodonaphthalene (1) with substituted alkenes and alkynes are useful for the synthesis of various acenaphthene and acenaphthylene derivatives. The reported reaction conditions are equally appropriate for catalyzed Ullmann reactions and for a domino-type annulation reaction leading to 9,10-diphenylphenanthrene (37).

Experimental Section

Melting point determinations are uncorrected. ^1H NMR spectra were recorded at 400.1 MHz using $CDCl_3$ as solvent and TMS as internal standard. ^{13}C NMR spectra were recorded at 100.6 MHz using $CDCl_3$ as solvent and as internal standard (δ = 77.05 ppm). High- and low-resolution mass spectra were recorded at an ionizing voltage of 70 eV by electron impact. 1,8-Diiodonaphthalene (1) was prepared as described by House.[18]

Palladium-Catalyzed Coupling Reactions of Aryl Iodides (General Procedure). The procedure for the preparation of *exo*-6b,7,8,9,10,10a-hexahydro-7,10-methanofluoranthene (16) is representative: A mixture of 1,8-diiodonaphthalene (1) (380 mg, 1.00 mmol), norbornene (15) (470 mg, 5.00 mmol), K_2CO_3 (1.1 g, 8.0 mmol), n-Bu_4NBr (645 mg, 2.00 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and DMF (10 mL) in a sealed tube (for convenience) is stirred under N_2 at 100 °C for 3 d. After diluting with water (50 mL) the reaction mixture is extracted three times with ether (50 mL). The ether extract is filtered through silica and concentrated. The crude product was purified by flash chromatography (hexane/silica gel) affording hydrocarbon 16 (208 mg, 94%): colorless solid; mp 65 °C (lit.[19] mp 66–68 °C).

All reactions were carried out on a 1-mmol scale in analogy to the foregoing procedure. The relative amounts of the reactants, the reaction time, and the isolated yields are given in the above schemes and tables. All new compounds (except 32) were fully characterized by spectroscopic means (IR, MS, NMR, UV). Selected data of the isolated products:

6b,12b-Dihydroacenaphth[1,2-*a*]acenaphthylene (5): colorless needles; mp 218 °C (ethanol; lit.[20] mp 216–219 °C); ^1H NMR δ 5.79 (s, 2 H), 7.48 (dd, J = 6.9, 8.2 Hz, 4 H), 7.60 ("d", "J" = 8.2 Hz, 4 H), 7.65 ("d", "J" = 6.9 Hz, 4 H); ^{13}C NMR δ 55.25 (s), 119.38 (d), 123.46 (d), 128.20 (d), 132.05 (s), 137.88 (s), 145.97 (s).

Acenaphth[1,2-*a*]acenaphthylene (8): dark purple crystals; mp 286 °C (CH_2Cl_2/pentane; lit.[4] mp 287–288 °C); ^1H NMR δ 7.59 (dd, J = 6.9, 8.1 Hz, 4 H), 7.80 ("d", "J" = 8.3 Hz, 4 H), 7.98 ("d", "J" = 6.8 Hz, 4 H); ^{13}C NMR: δ 123.21 (d), 127.61 (d), 127.78 (d), 129.19 (s), 133.49 (s), 134.17 (s), 144.52 (s).

1-(1-Naphthalenyl)acenaphthylene (12): yellow crystals; mp 91–92 °C (pentane); ^1H NMR δ 7.19 (s, 1 H), 7.42 (m, 1 H), 7.48–7.68 (m, 6 H), 7.74 ("d", "J" = 6.7 Hz, 1 H), 7.82–7.94 (m, 4 H), 8.26 ("d", "J" = 8.5 Hz, 1 H); ^{13}C NMR δ 124.09 (d), 124.47 (d), 125.48 (d), 125.90 (d), 125.95 (d), 126.59 (d), 127.12 (d), 127.30 (d), 127.60 (d), 127.64 (d), 128.01 (d), 128.03 (d), 128.32 (d), 128.37 (s), 128.45 (d), 128.78 (s), 132.22 (s), 134.00 (s), 134.04 (s), 139.40 (s), 140.50 (s), 142.31 (s); IR (KBr) 3046, 1428, 773 cm^{-1}; UV (acetonitrile) λ_{max} (lg ϵ) 218 nm (4.87), 324 (4.18), 408 (3.24); MS m/z (relative intensity) 279 (23), 278 (100, M$^+$), 277 (84), 276 (66), 107 (14), 57 (32). Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.79; H, 4.95.

Acenaphtho[1,2-*b*]benzo[*d*]furan (14):[21] orange needles; mp 85 °C (2-propanol); ^1H NMR δ 7.27–7.37 (m, 2 H), 7.53–7.62 (m, 3 H), 7.75 (dd, J = 0.7, 8.3 Hz, 1 H), 7.79–7.86 (m, 4 H); ^{13}C NMR δ 112.64 (d), 119.92 (d), 120.99 (d), 122.29 (d), 123.15 (s), 123.75 (d), 123.84 (d), 124.30 (s), 126.63 (d), 127.27 (s), 127.44 (d), 127.83 (d), 128.40 (d), 129.14 (s), 130.64 (s), 130.97 (s), 160.45 (s), 162.18 (s); IR (KBr) 3040, 1637, 1436, 1190, 815, 764, 731 cm^{-1}; UV (acetonitrile) λ_{max} (lg ϵ) 202 nm (4.62), 234 (4.70), 252 (4.35), 284 (4.26), 294 (4.28), 326 (4.07), 336 (3.96), 352 (3.81), 426 (3.15); MS m/z (relative intensity) 242 (100, M$^+$), 214 (44), 213 (75), 107 (30); HRMS m/z calcd for $C_{18}H_{10}O$ 242.0732, found 242.0731.

***exo*-6b,7,10,10a-Tetrahydro-7,10-methanofluoranthene (18)**: colorless oil;[22] ^1H NMR δ 0.92 ("d", "J" = 8.9 Hz, 1 H), 1.32 (m, 1 H), 2.93 (m, 2 H), 3.59 ("s", 2 H), 6.33 (m, 2 H), 7.28 ("d", "J" = 6.9 Hz, 2 H), 7.43 (dd, J = 6.9, 8.2 Hz, 2 H), 7.59 ("d", "J" = 8.2 Hz, 2 H); ^{13}C NMR δ 29.74 (t), 47.77 (d), 51.90 (d), 119.06 (d), 122.85 (d), 127.83 (d), 131.48 (s), 138.23 (d), 142.38 (s), 146.49 (s); MS m/z (relative intensity) 218 (6, M$^+$), 152 (100). Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.48; H, 6.47.

***exo,exo*-6b,7,7a,13b,14,14a-Hexahydro-7,14-methanoacenaphtho[1,2-*k*]fluoranthene (19)**: colorless crystals; mp >250 °C (pentane); ^1H NMR δ 0.56 ("s", 2 H), 2.60 (m, 2 H), 3.86 ("s", 4 H), 7.36 ("d", "J" = 6.9 Hz, 4 H), 7.47 (dd, J = 6.9, 8.2 Hz, 4 H), 7.60 ("d", "J" = 8.2 Hz, 4 H); ^{13}C NMR δ 27.27 (t), 48.96 (d), 53.67 (d), 119.34 (d), 122.77 (d), 128.07 (d), 131.13 (s), 141.00 (s), 147.26 (s); IR (KBr) 3041, 2944, 2919, 1599, 780 cm^{-1}; MS m/z (relative intensity) 344 (100, M$^+$), 192 (50), 191 (65), 178 (31), 165 (83), 153 (39), 152 (39). Anal. Calcd for $C_{27}H_{20}$: C, 94.15; H, 5.85. Found: C, 94.35; H, 5.90.

1,2-Dihydro-1-phenylacenaphthylene (21): colorless needles; mp 105 °C (lit.[23] mp 105–106 °C); ^1H NMR spectrum is in accord with reported data.[24]

(*E,E*)-1,8-Bis(2-phenylethenyl)naphthalene (22): colorless crystals; mp 144–146 °C (lit.[25] mp 146 °C); ^1H NMR spectrum is in accord with reported data.[25]

8,8′-Diiodo-1,1′-binaphthalene (23): pale yellow crystals; mp 147 °C; ^1H NMR δ 7.11 ("t", "J" = 7.6 Hz, 2 H), 7.32 (dd, J = 1.3, 7.1 Hz, 2 H), 7.48 (m, 2 H), 7.92–7.97 (m, 4 H), 8.23 (dd, J = 1.1, 6.3 Hz, 2 H); ^{13}C NMR δ 93.74 (s), 124.81 (d), 126.50 (d), 129.84 (d), 129.97 (d), 133.24 (s), 133.30 (d), 135.50 (s), 139.54 (s), 142.19 (d); IR (KBr) 3049, 1553, 1195, 819, 763 cm^{-1}; UV (acetonitrile) λ_{max} (lg ϵ) 226 nm (4.78), 292 (4.10), 304 (4.16), 314 (4.11), 408 (3.40), 434 (3.48); MS m/z (relative intensity) 506 (5, M$^+$), 253 (23), 252 (100), 250 (28), 126 (18), 125 (14). Anal. Calcd for $C_{20}H_{12}I_2$: C, 47.46; H, 2.39. Found: C, 47.47; H, 2.36.

1,2-Diphenylacenaphthylene (28): orange needles; mp 160 °C (hexane; lit.[26] mp 161–163 °C); ^1H NMR δ 7.27–7.38 (m, 6 H), 7.42–7.47 (m, 4 H), 7.58 (dd, J = 7.0, 8.0 Hz, 2 H), 7.73 ("d", "J" = 6.9 Hz, 2 H), 7.85 ("d", "J" = 8.1 Hz, 2 H); ^{13}C NMR: δ 124.02 (d), 127.14 (d), 127.33 (d), 127.86 (d), 128.28 (s), 128.41 (d), 128.47 (s), 130.11 (d), 135.30 (s), 138.16 (s), 140.01 (s); IR (KBr) 3060, 3024, 14.81, 1442, 1428, 821, 772, 749, 702 cm^{-1}; UV (acetonitrile) λ_{max} (lg ϵ) 236 nm (4.74), 250 (4.24), 262 (4.14), 322 (4.11), 334 (4.22), 346 (3.96), 4.22 (3.25); MS m/z (relative intensity) 305 (26), 304 (100, M$^+$), 303 (44), 302 (38). Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.90; H, 5.24.

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(18) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003.

(19) Oliver, M. J.; Patney, H. K.; Paddon-Row, M. N. *Aust. J. Chem.* **1980**, *33*, 795.

(20) Agosta, W. C. *J. Am. Chem. Soc.* **1967**, *89*, 3505.

(21) The HH COSY featuring two 3-spin and one 4-spin system is consistent with the assigned structure.

(22) Baker, R.; Mason, T. J. *J. Chem. Soc. C* **1970**, 596.

(23) Brown, B. R.; Hammick, D. L. *J. Chem. Soc.* **1948**, 1395.

(24) Fay, C. K.; Grutzner, J. B.; Johnson, L. F.; Sternhell, S.; Westerman, P. W. *J. Org. Chem.* **1973**, *38*, 3122.

(25) Meier, H.; Prass, E.; Zertani, R.; Eckes, H.-L. *Chem. Ber.* **1989**, *122*, 2139.

(26) Card, P. J.; Friedli, F. E.; Shechter, H. *J. Am. Chem. Soc.* **1983**, *105*, 6104.

1-(2-Methylphenyl)-2-phenylacenaphthylene (30): orange needles; mp 106–107 °C (pentane); ^{1}H NMR δ 2.01 (s, 3 H), 7.20–7.45 (m, 10 H), 7.54 (dd, J = 6.9, 8.3 Hz, 1 H), 7.61 (dd, J = 6.9, 8.0 Hz, 1 H), 7.82–7.88 (m, 3 H); IR (KBr) 3057, 3036, 1481, 1428, 765, 748, 727, 703 cm^{-1}; UV (acetonitrile) λ_{max} (lg ϵ) 236 nm (4.74), 248 (4.16), 262 (4.10), 276 (4.03), 320 (4.10), 332 (4.21), 346 (3.92), 416 (3.23); MS *m/z* (relative intensity) 318 (100, M$^+$), 317 (23), 313 (20), 312 (19), 240 (25), 239 (45). Anal. Calcd for $C_{25}H_{18}$: C, 94.30; H, 5.70. Found: C, 94.22; H, 5.70.

1,2-Dipropylacenaphthylene (32): yellow oil; slightly impure according to ^{1}H NMR, containing 13% of an isomer with one exocyclic double bond; ^{1}H NMR δ 1.02 (t, J = 7.4 Hz, 6 H), 1.71 (m, 4 H), 2.70 (m, 4 H), 7.45 (m, 2 H), 7.51 (m, 2 H), 7.66 (m, 2 H); ^{13}C NMR δ 14.47 (q), 24.13 (t), 27.97 (t), 120.93 (d), 125.99 (d), 127.47 (d), 127.78 (s), 128.57 (s), 138.35 (s), 141.21 (s); MS *m/z* (relative intensity) 236 (41, M$^+$), 207 (100), 193 (31), 178 (45), 165 (32).

1,2-Acenaphthylenedicarboxylic acid dimethyl ester (34): yellow solid; mp 102 °C (lit.[27] mp 105–106 °C); ^{1}H NMR δ 4.01 (s, 6 H), 7.64 (dd, J = 7.0, 8.1 Hz, 2 H), 7.97 ("d", "J" = 8.1 Hz, 2 H), 8.13 ("d", "J" = 7.0 Hz, 2 H); ^{13}C NMR δ 52.33 (q), 127.03 (s), 128.26 (d), 128.35 (d), 128.51 (s), 130.34 (d), 134.54 (s), 135.10 (s), 165.11 (s).

7-Phenylbenzo[*k*]fluoranthene (36): pale yellow plates; mp 140 °C (ether/2-propanol; lit.[14] mp 157–159 °C; lit.[28] mp 166–167 °C); ^{1}H NMR δ 6.63 ("d", "J" = 7.0 Hz, 1 H), 7.33 (dd, J = 7.2, 8.1 Hz, 1 H), 7.39 (m, 1 H), 7.47–7.53 (m, 3 H), 7.58–7.70 (m, 5 H), 7.73 ("d", "J" = 8.2 Hz, 1 H), 7.82 ("d", "J" = 8.1 Hz, 1 H), 7.99 ("d", "J" = 8.6 Hz, 1 H), 8.07 ("d", "J" = 6.9 Hz, 1 H), 8.38 (s, 1 H); ^{13}C NMR: δ 119.06 (d), 119.83 (d), 122.13 (d), 125.90 (d), 125.93 (d), 125.95 (d), 126.26 (d), 126.85 (d), 127.93 (d), 127.97 (d), 128.13 (d), 128.69 (d), 129.16 (d), 129.94 (d), 130.35 (s), 133.05 (s), 133.30 (s), 135.24 (s), 135.36 (s), 135.43 (s), 136.50 (s), 137.04 (s), 137.40 (s), 138.70 (s); IR (KBr) 3031, 1609, 1433, 822, 798, 777, 749, 702 cm^{-1}; UV (acetonitrile) λ_{max} (lg ϵ) 216 nm (4.64), 244 (4.73), 248 (4.73), 268 (4.33), 288 (4.32), 298 (4.58), 308 (4.70), 326 (3.89), 338 (3.79), 364 (3.78), 382 (4.05), 404 (4.07); MS *m/z* (relative intensity) 329 (29), 328 (100, M$^+$), 327 (34), 326 (35), 163 (28). Anal. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 95.09; H, 4.90.

9,10-Diphenylphenanthrene (37): colorless needles; mp 236–238 °C (ether; lit.[17] mp 236–237 °C); NMR spectra are in accord with reported data.[17]

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(27) Herold, D. A.; Rieke, R. D. *J. Org. Chem.* **1979**, *44*, 1359.

(28) Bossenbroek, B.; Sanders, D. C.; Curry, H. M.; Shechter, H. *J. Am. Chem. Soc.* **1969**, *91*, 371.