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Intramolecular Dehydro Diels−Alder Reactions of Diarylacetylenes: Switching between Benzo[*b*]- and Benzo[*c*]fluorenones as Products by Controlling the Rearrangement of Cyclic Allene Intermediates

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Thermal cyclization of 1-[2-(arylethynyl)phenyl]-3-trimethylsilylpropynones affords a mixture of benzo[*b*]fluorenones and benzo[*c*]fluorenones. The ratio of the two isomers can be efficiently varied between 100:0 and 0:100 by introducing substituents with appropriate electronic and steric properties on the aryl rings and using an appropriate solvent.

Introduction

Intramolecular dehydro Diels−Alder reactions between alkynes and arenynes are well-known processes,[1] some having first been reported in the 19th century. The intermediates in these reactions are 1,2,4-cyclohexatrienes, strained cyclic allenes[2] that normally evolve to aromatic products by isomerization.[3] Echavarren's group[4] and ours[5] have recently reported that isonaphthalenes (a class of cyclic allenes) can undergo electrocyclic rearrangement to isomeric isonaphthalenes via 1,2-dehydro[10]annulenes. As a result, thermal cyclization of propynone **1a** ($R^1 = R^2 = R^3 = H$), for example, followed by selective desilylation, affords a mixture of benzo[*b*]fluorenone **3a** (R = H), in which a 2-phenylnaphthalene skeleton arises from direct aromatizing isomerization of the initial [4 + 2] cyclization product **2a** and benzo[*c*]fluorenone **7a**,[6] in which a 1-phenylnaphthalene skeleton arises through a six-electron electrocyclic opening of **2a** to (5*Z*,7*Z*)-1,2-dehydro[10]annulene **4a**, isomerization of the latter to (5*E*,7*E*)-1,2-dehydro[10]annulene **5a** by simultaneous rotation of the C5−C6 and C7−C8 bonds, [1,6]-electrocyclization of **5a** to the new cyclic allene **6a**, and final aromatizing isomerization of this allene (Scheme 1). With **1a**, or analogues in which the terminal TMS is replaced with other SiR_3 groups,[4,5b,7] the rearrangement product **7** is usually the minor product, but results with other arylpropynones[4] suggested to us that the yield of **7** might increase with an electron-rich substituent in the arylethynyl moiety. In this paper, we report the synthesis of several benzo[*b*]-, benzo[*c*]-, and dibenzo[*b*,*g*]fluorenones in the course of a systematic study of how steric and electronic effects of arylethynyl substitution influence the **2**:**6** ratio in the thermal cyclization of 1-[2-(arylethynyl)-phenyl]-3-trimethylsilylpropynones **1b**−**o**.[8]

Results and Discussion

Trimethylsilylpropynones **1b**−**e**, in which the terminal aryl ring has a single substituent in the para position, were synthesized in two steps by Sonogashira coupling of alkyne **8**[9] or **9**[10] with the appropriate aryl iodide (**10b**−**e**)[11] followed by oxidation of the propargylic alcohols with activated MnO_2 (Scheme 2).

Thermal cyclization, carried out by heating solutions of **1a**−**e** in freshly distilled toluene at 150 °C in an argon-filled sealed tube, afforded inseparable mixtures of silylated benzofluorenones **3′a**−**e** (Scheme 1) and **7a**−**e**,[12] but selective removal of the TMS group of **3′** by reaction with

(1) (a) Michael, A.; Bucher, J. E. *Chem. Ber.* **1895**, *28*, 2511−2512. (b) Danheiser, R. L.; Gould, A.; Fernández de la Pradilla, R.; Helgason, A. L. *J. Org. Chem.* **1994**, *59*, 5514−5515. (c) Burrell, R. C.; Daoust, K. J.; Bradley, A. Z.; DiRico, K. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1996**, *118*, 4218−4219. (d) Schmittel, M.; Strittmatter, M.; Schemk, W. A.; Hagel, M. *Z. Naturforsch.* **1998**, *53b*, 1015−1020.

(2) For a review of the reactivities and structures of cyclic allenes, see: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111−1124.

(3) (a) Rodríguez, D.; Navarro, A.; Castedo, L.; Domínguez, D.; Saá, C. *Org. Lett.* **2000**, *2*, 1497−1500. (b) Rodríguez, D.; Navarro-Vázquez, A.; Castedo, L.; Domínguez, D.; Saá, C. *J. Org. Chem.* **2003**, *68*, 1938−1946.

(4) Atienza, C.; Mateo, C.; de Frutos, Ó.; Echavarren, A. M. *Org. Lett.* **2001**, *3*, 153−155.

(5) (a) Rodríguez, D.; Navarro-Vázquez, A.; Castedo, L.; Domínguez, D.; Saá, C. *J. Am. Chem. Soc.* **2001**, *123*, 9178−9179. (b) Rodríguez, D.; Navarro-Vázquez, A.; Castedo, L.; Domínguez, D.; Saá, C. *Tetrahedron Lett.* **2002**, *43*, 2717−2720.

(6) Benzo[*c*]fluorene derivatives have been postulated as carcinogenic metabolites: Wang, J.-Q.; Weyand, E. H.; Harvey, R. G. *J. Org. Chem.* **2002**, *67*, 6216−6219.

(7) Tertiary alcohols gave only **3**, and *tert*-butyl gave **3** and **7** in a 16:1 ratio.

(8) On electronic control in the Schmittel and Bergman cyclizations, see: (a) Schmittel, M.; Maywald, M. *Chem. Commun.* **2001**, 155−156. (b) Jones, G. B.; Warner, P. M. *J. Am. Chem. Soc.* **2001**, *123*, 2134−2145. (c) Choy, N.; Kim, C.-S.; Ballestero, C.; Artigas, L.; Diez, C.; Lichtenberger, F.; Shapiro, J.; Russell, K. C. *Tetrahedron Lett.* **2000**, *41*, 6955−6958. Schmittel, M.; Kiau, S. *Chem. Lett.* **1995**, 953−954.

(9) Brückner, R. *Synlett* **1994**, 51−53; *Liebigs Ann.* **1996**, *C41*, 447−456 and 457−471.

(10) Chang, J.; Baik, J.; Lee, C.; Han, M.; Hong, S.-K. *J. Am. Chem. Soc.* **1997**, *119*, 3197−3198.

(11) For synthesis of desilylated **10d**, see: Rucker, M.; Brückner, R. *Tetrahedron Lett.* **1997**, *38*, 7353−7356.

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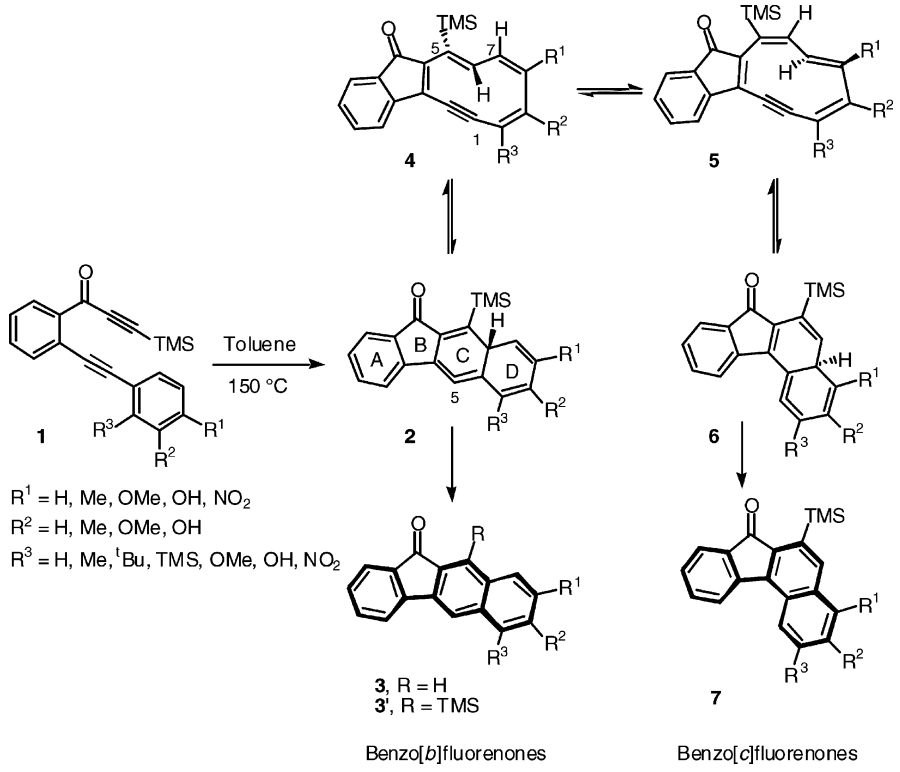
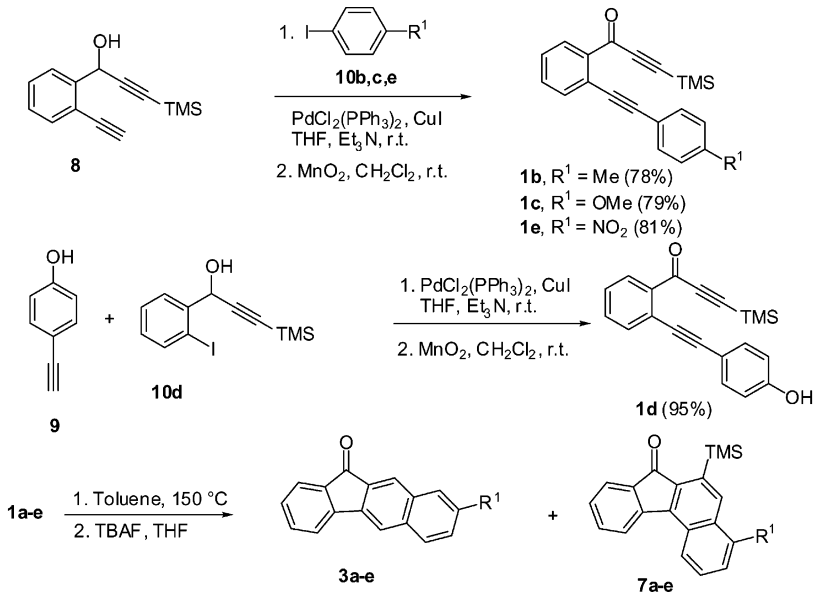
SCHEME 1. Intramolecular Dehydro Diels–Alder of Propynones 1



SCHEME 2. General Conditions for the Synthesis and Thermolysis of Propynones 1a–e



tetrabutylammonium fluoride solution in THF[5b] allowed the isolation of silylated benzo[*c*]fluorenones **7a–e** and desilylated benzo[*b*]fluorenones **3a–e** (Scheme 2 and Table 1). Propynone **1a** (R^1 = H) gave a 23% yield of **7a** and a 59% yield of **3a** (entry 1).[5b] The **7**:**3** ratio was higher with the electron-donating substituent Me of **1b** (although the total yield decreased; entry 2) and was further increased by the methoxy group of **1c**, confirming that it tends to increase with the electron-donating capacity of R^1 (entry 3). Although the even more powerful electron donor of **1d** afforded only the linear benzo[*b*]fluorenone **3d** (entry 4), this is thought likely to have been due to competitive intermolecular protonation of position 5 of the initial cyclic allene **2d** by the acidic phenolic proton.[5a,13,14] Compound **1e**, with its electron-withdrawing nitro group, was smoothly converted to benzo[*b*]fluo-

(12) In the case of **1d** (R^1 = OH) and **1e** (R^1 = NO_2), silylated benzofluorenones **3′d** (30%) and **3′e** (80%) were the only products obtained. Attempts to desilylate these compounds led to decomposition.

(13) Relatively low yield obtained (30%) might be due to the moderate thermal instability of **1d**.

(14) Lithium, potassium, and sodium phenoxides of **1d** were prepared by treatment with LDA, K_2CO_3, and NaH, respectively, but attempts at their cyclization all failed because they were thermally unstable and decomposed.

SCHEME 3. Thermal Cyclization of Propynones 1f−h

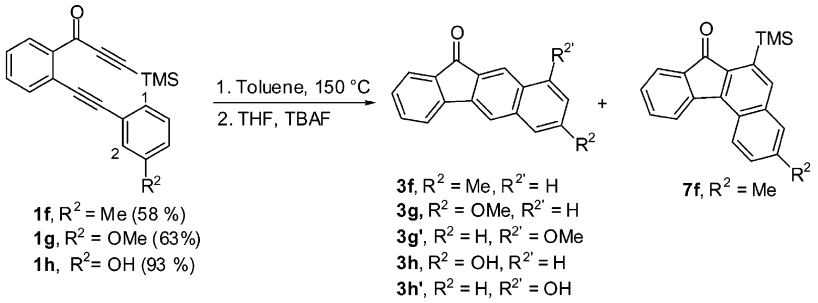


TABLE 1. Thermal Cyclization of Silylpropynones 1a−l

entry	propynone	aryl ring substituent	benzo[*b*]-fluorenone **3** (%)	benzo[*c*]-fluorenone **7** (%)[a]	ratio of **3**:**7**
1	**1a**		59	23	2.6:1
2	**1b**	*p*-Me	33	22	1.5:1
3	**1c**	*p*-OMe	31	30	1:1
4	**1d**	*p*-OH	30[b]		1:0
5	**1e**	*p*-NO_2	80[b]		1:0
6	**1f**	*m*-Me	52	7	7.4:1
7	**1g**	*m*-OMe	59[c]		1:0
8	**1h**	*m*-OH	44[b,c]		1:0
9	**1i**	*o*-Me	27	34	1:1.3
10	**1j**	*o*-OMe	39	17	2.3:1
11	**1k**	*o*-^{t}Bu		56	0:1
12	**1k**[d]	*o*-^{t}Bu	52[e]		1:0
13	**1l**	*o*-TMS		36	0:1

[a] Isolated yields after desilylation. [b] Yields of **3′d**, **3′e**, and **3′h**, respectively. [c] **3g′** and **3h′** were obtained in 8 and 6% yields, respectively. [d] Reaction carried out in Et_3N as a solvent. [e] Yield of **3′k**.

renone **3e** without any production of **7e**. From the results, it seems evident that electronic effects in the reacting aromatic ring affect largely the regioselectivity of the reaction since the fate of the first-formed allenic cycloadduct **2** depends on the nature of the substituent at the terminal phenyl ring as well as on the nature of the reaction medium.[15] Specifically, the proton at the junction of rings C and D of **2** is somewhat acidic (the C−H bond is conjugated with the carbonyl group and with a dienic system). Electron-withdrawing substituents would favor a fast deprotonation and the consequent aromatization of rings C and D to give **3**. Electron-releasing substituents would retard the deprotonation process, making competitive the thermal electrocyclic opening of the C and D rings to **4** and its isomerization to **5** (this is favored also by a substantial decrease of strain). Finally, the latter electrocyclizes to give the more stable allenic adduct **6** from which **7** is formed by the deprotonation−aromatization process.

We next prepared substrates **1f**−**h**, which have meta-substituted terminal rings.[16] The major isolated products of their cyclization were benzo[*b*]fluorenones **3f**,**g**, which were obtained in 52 and 59%, respectively, and **3′h**,[17] obtained in 44% yield (Scheme 3). The minor products were the rearranged benzo[*c*]fluorenone **7f** (7%) and the benzo[*b*]fluorenones **3g′** and **3h′** (8 and 6%, respectively),

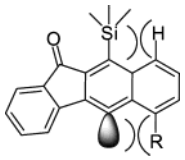


FIGURE 1. Steric interactions in allenes **2i**−**l**.

these latter being derived from cycloaddition at the more crowded position 2 of the aromatic ring (Scheme 3). In the case of **1h**, the failure to obtain **7h** is again probably due to the acidic phenolic proton favoring aromatization of the initial cyclic allene **2h**. Phenoxide derivatives of **1h** were thermally unstable and could not be cyclized. As before, the deprotonation−aromatization of the initial allene **2** is the most favored pathway irrespective of the nature of the electron-releasing meta substituent in **1**.

We then prepared the 1-[2-(arylethynyl)phenyl]-3-trimethylsilylpropynones **1i**−**l** to evaluate what were expected to be the mainly steric effects of ortho substitution. The terminal trimethylsilyl group of compounds **1** had previously been reported to increase the amount of rearranged product due to steric repulsion in allene **2** between the TMS and the peri hydrogen, and it was hoped that ortho substitution on the arylethynyl ring would further favor rearrangement due to repulsion between the ortho group and the electron pair of the central carbon of the allene (Figure 1).

Propynones **1i**−**l** were synthesized following the same procedure as described above (Scheme 4).[16] Gratifyingly, cyclization of the *o*-methyl derivative **1i** in toluene at 150 °C, followed by selective desilylation, afforded a higher yield of the rearranged benzo[*c*]fluorenone **7i** than of the benzo[*b*]fluorenone **3i**, 34 vs 27%. However, in the case of a better electron-releasing substituent, the *o*-methoxy derivative **1j**, the benzo[*b*]fluorenone was once again the major product (39 vs 17% of the benzo[*c*]fluorenone **7j**). Unfortunately, analogues of **1** with more electron-rich or electron-poor ortho susbstituents (R^3 = OH or NO_2, respectively) could not be cyclized due to thermal instability, but the steric origin of the tendency of **2i** to rearrange appeared to be confirmed when the *tert*-butyl and trimethylsilyl analogues **1k** and **1l** afforded only the rearranged benzo[*c*]fluorenones **7k** and **7l**[18] (in 56 and 36% yields, respectively); this is the first time that only the rearranged products have been obtained due, most probably, to the steric hindrance for protonation of the corresponding allenes **2** (Scheme 4). Remarkably, how-

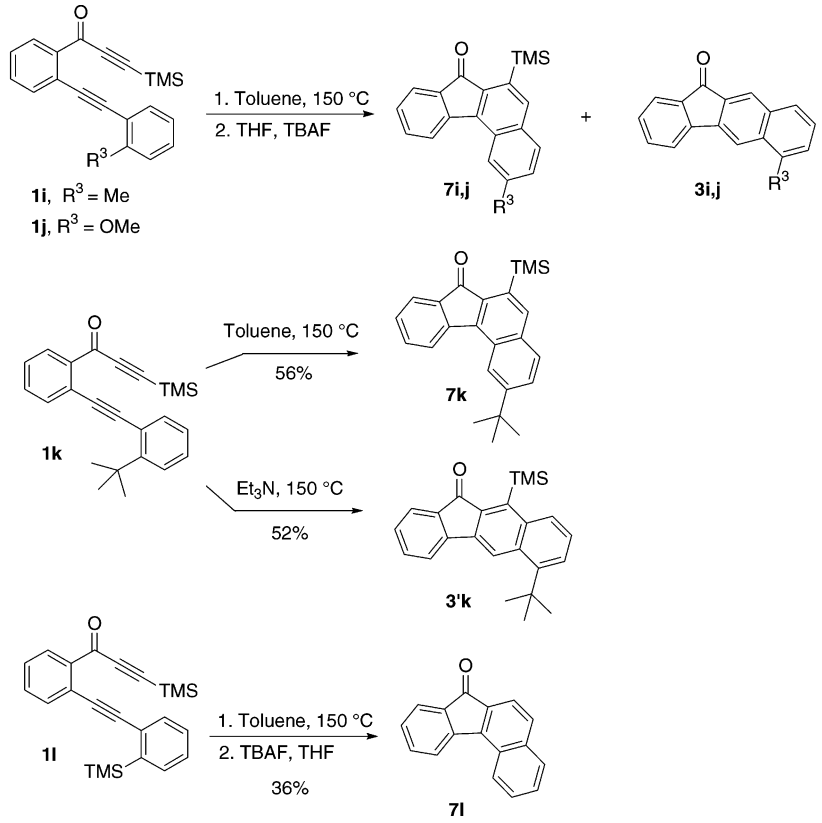
(15) Thermolysis of **1a** in the presence of triethylamine gives **3a** quantitatively; see ref 5b.

(16) Compounds **1f**−**o** were all prepared in good yields by procedures similar to the one depicted in Scheme 2. See Supporting Information for details.

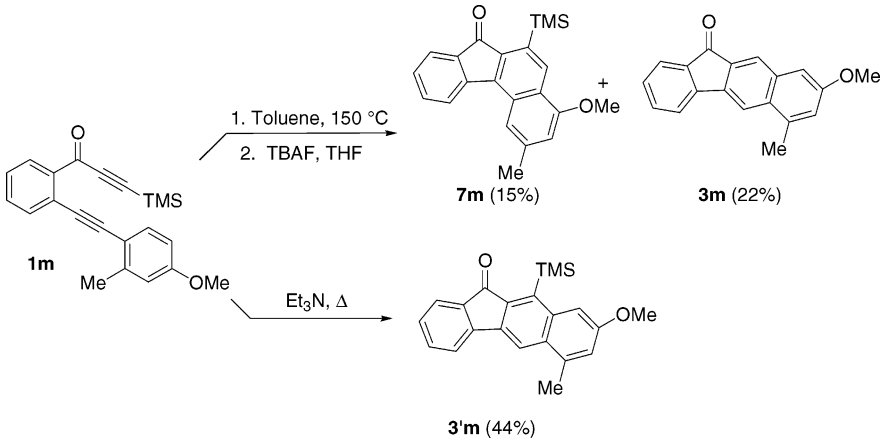
(17) No desilylation step was necessary in this case.

(18) Campo, M. A.; Larock, R. C. *J. Org. Chem*. **2002**, *67*, 5616−5620.

SCHEME 4. Neutral and Basic Thermal Cyclizations of Propynones 1i–l



SCHEME 5. Neutral and Basic Thermal Cyclization of Propynone 1m

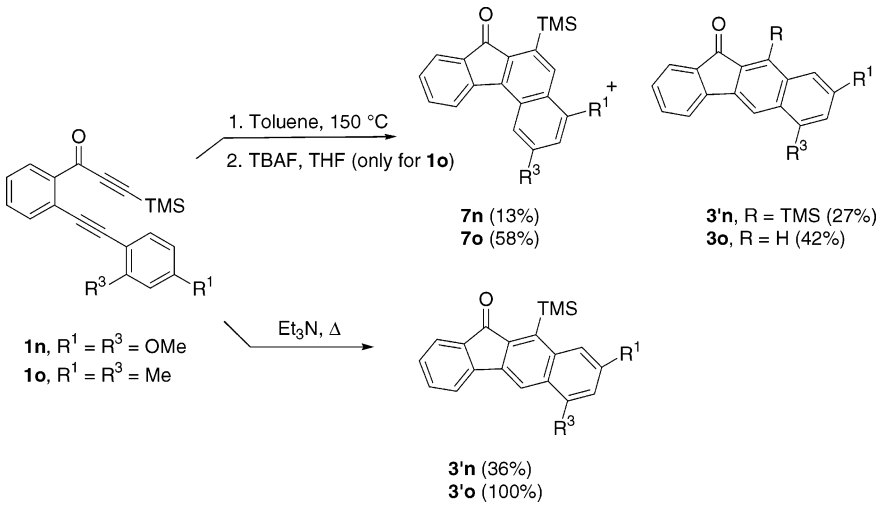


ever, when the thermolysis of **1k** was carried out in triethylamine as a solvent instead of toluene,[5b] the only product isolated was benzo[*b*]fluorenone **3′k** (52%), doubtless due to the acidic nature of the proton at the junction of rings C and D of **2** and the basic nature of triethylamine. Thus, endowing the reacting phenyl group with bulky ortho substituents subject to steric interaction with the lone pair of the cyclic allene intermediate seems to allow either the benzo[*b*]- or the benzo[*c*]fluorenone skeleton to be obtained selectively by just using the appropriate solvent.

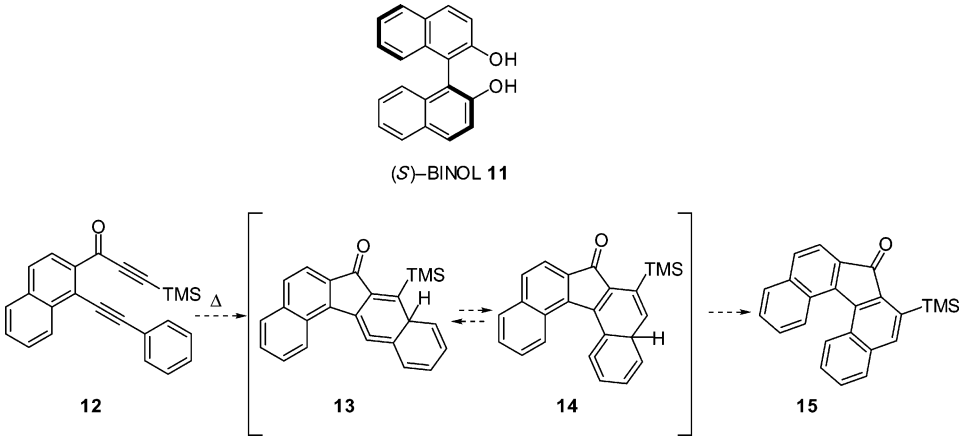
To test the effects of two substituents on the reacting aryl ring, we first synthesized the diarylacetylene **1m** (Scheme 5) in the hope that the combined effects of the sterically demanding ortho susbstituent and the electron-donating *p*-methoxy group might shift the **3**:**7** ratio toward **7** more than the *o*-Me group by itself. However, the reaction gave a relatively low global yield of **7** and **3** in 1:1.5 ratio, indicating that the expected combination of effects had not occurred. Thermolysis of diarylacetylene **1n**, in which the terminal aryl ring has *o*- and *p*-methoxy susbstituents, gave similar results (no desilylation is needed for separation of both isomers, Scheme 6). Diarylacetylene **1o**, in which the substituents are two methyls, afforded an excellent yield, but the **7**:**3** ratio, 1.4:1, hardly improved on that obtained with the single methyl of **1i** (entry 8 in Table 1). Thermolysis of diarylacetylenes **1n**–**o** in Et_3N gave the expected benzo[*b*]-fluorenones **3′n**–**o** in moderate to excellent yields.[3]

1,1′-Binaphthalene derivatives such as (*S*)-BINOL **11**[19] occupy a prominent position among C_2-symmetric chiral auxiliaries and ligands for asymmetric synthesis.[20] In an

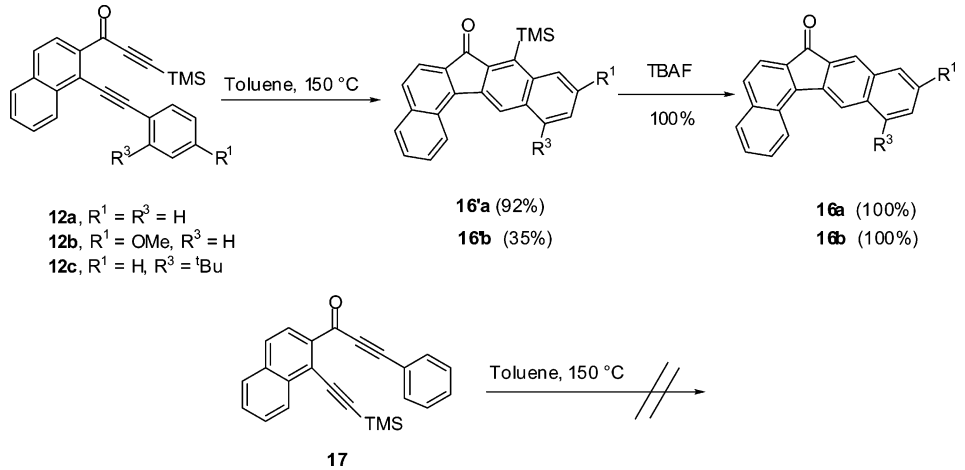
SCHEME 6. Neutral and Basic Thermal Cyclizations of Propynones 1n−o



SCHEME 7. Hypothetical Mechanistic Course for the Thermolysis of Naphthyl Phenylacetylene 12



SCHEME 8. Thermal Cyclization of Propynones 12a−c



attempt to apply the methods described above to the synthesis of 1,1′-binaphthalene **15**, we subjected naphthyl phenylacetylene **12** to thermolysis under neutral conditions, hoping that rearrangement of the initial allene **13** to **14** would lead to the desired product (Scheme 7).

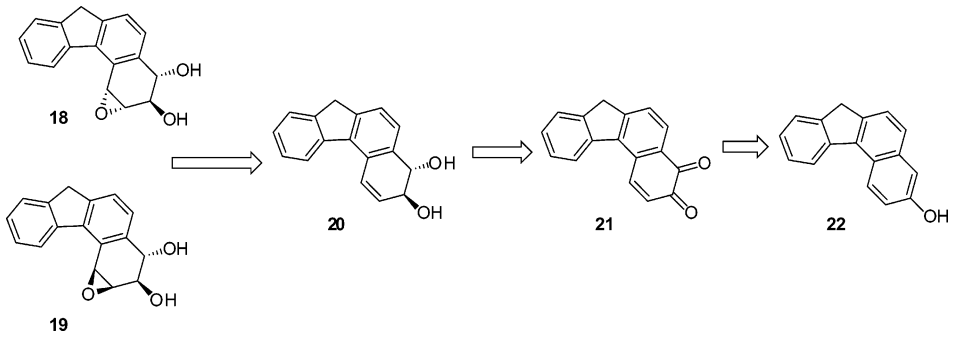
Somewhat surprisingly, heating a solution of **12a** in toluene at 150 °C gave exclusively the silylated dibenzo[*b*,*g*]fluoren-7-one **16′a** in an excellent 92% yield (Scheme 8), being a novel route to access this interesting aromatic nucleus[21] (desilylation of **16′a** then gave the parent

(19) For a review of BINOL derivatives, see: Chen, Y.; Yekta, S.; Yudin, A. K. *Chem. Rev.* **2003**, *103*, 3155−3211.

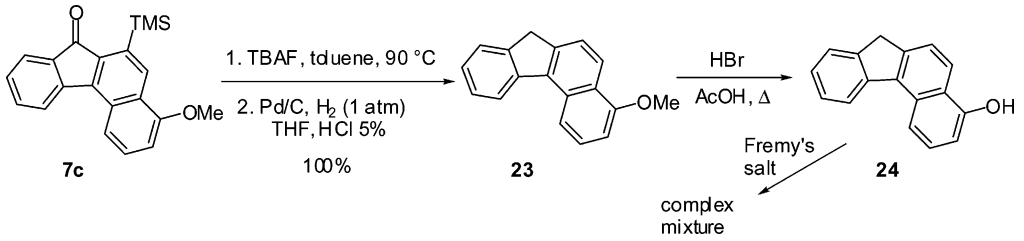
(20) For a review of C_2 symmetry in asymmetric synthesis, see: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.

(21) For old methods based on cyclodehydration of β-aryl ketones, see: (a) Colonge, J.; Weinstein, G. *Bull. Soc. Chim. Fr.* **1951**, 961−965. (b) Lambert, P.; Martin, R. H. *Bull. Soc. Chim. Belg.* **1952**, *61*, 132−138. (c) Martin, R. H. *Helv. Chim. Acta* **1947**, *30*, 620−627.

SCHEME 9. Retrosynthetic Analysis of Carcinogenic Benzo[*c*]fluorene Diepoxides 18 and 19 from Phenol 22



SCHEME 10. Attempted Route to Carcinogenic Benzo[*c*]fluorene Metabolites from Benzo[*c*]fluorenic Phenol 24



member of the series, **16a**, in 95% yield).[21c] Allene **13** must therefore aromatize much more readily than it rearranges to the cyclic allene **14**. Attempts to invert this preference by the same means as had proved successful for allene **2**, i.e., by furnishing the terminal aryl ring of the starting compound with substituents with appropriate electronic and steric properties, were in this case unsuccessful: **12b** gave only a 35% yield of **16′b**, and **12c** underwent slow decomposition. Thermolysis of naphthylphenylpropynone **17** under the same conditions gave only unaltered starting material (Scheme 8).

Harvey et al. have recently described the synthesis of the diepoxides **18** and **19**, which are suspected of being the ultimate carcinogenic metabolites of 7*H*-benzo[*c*]-fluorene (BcF), a coal tar component implicated in the causation of lung tumors.[6] These metabolites can be obtained by epoxidation of diol **20**, which is in turn derived from phenol **22** in two steps via the *o*-quinone intermediate **21** (Scheme 9).

We wondered whether the previously synthesized benzo[*c*]fluorenone **7c** might also be convertible into the *o*-quinone intermediate **21**. However, although desilylation of **7c** followed by hydrogenation over a palladium–charcoal catalyst gave **23** in quantitative yield, and **23** was smoothly converted to phenol **24** by heating with 48% HBr in acetic acid (Scheme 10), oxidation of **24** with Fremy's salt [$(SO_3K)_2NO$] gave only a complex mixture of products, probably due to the position para to the −OH group being substitutable.[22]

In summary, a theoretical and experimental study of the cyclization of compounds **1** shows that there is a relationship between the electron-richness of the reacting aryl group (determined by its para substituent) and the extent of rearrangement of allene **2** to allene **6**. Meta substituents, whatever their electronic nature, favor the aromatization of **2** to benzo[*b*]fluorenones **3**. Substitution in the ortho position allows the choice of solvent to determine whether rearranged or unrearranged products are obtained. Dibenzo[*b*,*g*]fluoren-7-ones can be obtained efficiently by thermolysis of naphthylarylacetylenes in neutral conditions.

Experimental Section

Thermal Cyclizations: General Procedure. A toluene or toluene/Et_3N (8:0.5) solution of the substrate (c = 20–65 mM) was placed in a sealed tube and heated overnight at 150 °C in a silicon oil bath. After evaporation of the solvent, the crude material was purified by column chromatography on silica gel using a mixture of hexanes/EtOAc (typically, 6:1) as the eluent.

8-Methylbenzo[*b*]fluoren-11-one 3b: yellow prisms; mp 144–146 °C; ^{1}H NMR ($CDCl_3$) δ 8.08 (s, 1H, Ar*H*), 7.82 (s, 1H, Ar*H*), 7.76–7.73 (m, 4H, Ar*H*), 7.55 (td, J = 7.5, 1.3 Hz, 1H, Ar*H*), 7.38 (dd, J = 8.3, 1.6 Hz, 1H, Ar*H*), 7.32 (td, J = 7.6, 1.0 Hz, 1H, Ar*H*), 2.50 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ 193.2 (*C*O), 144.9 (*C*), 137.5 (*C*), 136.8 (*C*), 136.0 (*C*), 134.9 (*C*), 134.9 (*C*H), 133.7 (*C*), 132.7 (*C*), 131.0 (*C*H), 129.9 (*C*H), 128.8 (*C*H), 128.5 (*C*H), 125.0 (*C*H), 124.3 (*C*H), 120.7 (*C*H), 118.8 (*C*H), 21.5 (*C*H_3); MS (70 eV) m/z (%) 244 (M^+, 100), 215 (41).

7-Methylbenzo[*b*]fluoren-11-one 3f: yellow prisms; mp 150–152 °C; ^{1}H NMR ($CDCl_3$) δ 8.11 (s, 1H, Ar*H*), 7.88–7.65 (m, 4H, Ar*H*), 7.58 (s, 1H, Ar*H*), 7.54 (td, J = 7.5, 0.9 Hz, 1H, Ar*H*), 7.36–7.26 (m, 2H, Ar*H*), 2.51 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ 193.0 (*C*O), 144.7 (*C*), 139.2 (*C*), 138.3 (*C*), 137.0 (*C*), 136.1 (*C*), 134.7 (*C*H), 131.9 (*C*), 131.6 (*C*), 130.4 (*C*H), 128.9 (2x*C*H), 128.0 (*C*H), 125.3 (*C*H), 124.2 (*C*H), 120.8 (*C*H), 118.3 (*C*H), 21.8 (*C*H_3); MS (70 eV) m/z (%) 244 (M^+, 100), 215 (56).

6-Methylbenzo[*b*]fluoren-11-one 3i: yellow prisms; mp 154–155 °C; ^{1}H NMR ($CDCl_3$) δ 8.10 (s, 1H, Ar*H*), 7.95 (s, 1H, Ar*H*), 7.75–7.66 (m, 3H, Ar*H*), 7.52 (t, J = 7.3 Hz, 1H, Ar*H*), 7.39–7.22 (m, 3H, Ar*H*), 2.67 (s, 3H, CH_3); ^{13}C NMR/DEPT ($CDCl_3$) δ 193.2 (*C*O), 145.0 (*C*), 138.2 (*C*), 136.1 (*C*), 135.9 (*C*), 135.2 (*C*), 134.9 (*C*H), 133.7 (*C*), 132.2 (*C*), 130.0 (*C*H), 129.2 (*C*H), 129.1 (*C*H), 126.6 (*C*H), 126.1 (*C*H), 124.4 (*C*H), 120.8

(22) Martin Owton, W. *J. Chem. Soc., Perkin Trans.* **1999**, 2409–2420.

(*C*H), 115.3 (*C*H), 19.6 (*C*H_3); MS (70 eV) *m*/*z* (%) 244 (M^+, 100), 243 (25), 215 (46).

4-Methyl-6-(trimethylsilyl)benzo[*c*]fluoren-7-one 7b: orange prisms; mp 165−167 °C; ^{1}H NMR ($CDCl_3$) δ 8.40 (d, J = 8.1 Hz, 1H, Ar*H*), 8.16 (s, 1H, Ar*H*), 8.05 (d, J = 7.6 Hz, 1H, Ar*H*), 7.68−7.63 (m, 1H, Ar*H*), 7.56−7.40 (m, 3H, Ar*H*), 7.30 (t, J = 7.4 Hz, 1H, Ar*H*), 2.74 (s, 3H, CH_3), 0.45 (s, 9H, Si(CH_3)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ 195.9 (*C*O), 145.2 (*C*), 143.4 (*C*), 136.0 (*C*), 135.8 (*C*), 135.6 (*C*), 134.6 (*C*), 134.3 (*C*H), 134.2 (*C*), 132.8 (*C*H), 129.4 (*C*), 129.2 (*C*H), 128.5 (*C*H), 127.7 (*C*H), 123.7 (*C*H), 123.4 (*C*H), 122.8 (*C*H), 20.1 (*C*H_3), −0.9 (Si(*C*H_3)$_3$); MS (70 eV) *m*/*z* (%) 316 (M^+, 10), 302 (33), 301 (100).

3-Methyl-6-(trimethylsilyl)benzo[*c*]fluoren-7-one 7f: orange prisms; mp 134−136 °C; ^{1}H NMR ($CDCl_3$) δ 8.39 (d, J = 8.5 Hz, 1H, Ar*H*), 8.01 (d, J = 7.9 Hz, 1H, Ar*H*), 7.85 (s, 1H, Ar*H*), 7.69−7.62 (m, 2H, Ar*H*), 7.55−7.42 (m, 2H, Ar*H*), 7.34−7.25 (m, 1H, Ar*H*), 2.54 (s, 3H, CH_3), 0.43 (s, 9H, Si(CH_3)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ 195.8 (*C*O), 145.0 (*C*), 143.1 (*C*), 138.5 (*C*), 137.1 (*C*), 136.3 (*C*H), 135.2 (*C*), 135.1 (*C*), 134.3 (*C*), 134.2 (*C*), 130.3 (*C*H), 128.7 (*C*H), 128.5 (*C*H), 127.3 (*C*H), 124.3 (*C*H), 123.6 (*C*H), 123.1 (*C*H), 21.8 (*C*H_3), −0.9 (Si(*C*H_3)$_3$); MS (70 eV) *m*/*z* (%) 316 (M^+, 7), 301 (100).

2-Methyl-6-(trimethylsilyl)benzo[*c*]fluoren-7-one 7i: orange prisms; mp 172−174 °C; ^{1}H NMR ($CDCl_3$) δ 8.16 (s, 1H, Ar*H*), 7.97 (d, J = 7.4 Hz, 1H, Ar*H*), 7.85 (s, 1H, Ar*H*), 7.73 (d, J = 7.7 Hz, 1H, Ar*H*), 7.60 (d, J = 7.2 Hz, 1H, Ar*H*), 7.47 (t, J = 7.6 Hz, 1H, Ar*H*), 7.36 (d, J = 6.7 Hz, 1H, Ar*H*), 7.25 (t, J = 7.4 Hz, 1H, Ar*H*), 2.55 (s, 3H, CH_3), 0.44 (s, 9H, Si(CH_3)$_3$); ^{13}C NMR/DEPT ($CDCl_3$) δ 195.9 (*C*O), 145.1 (*C*), 142.3 (*C*), 137.9 (*C*), 136.8 (*C*H), 135.9 (*C*), 135.1 (*C*), 134.2 (*C*H), 134.1 (*C*), 133.8 (*C*), 130.5 (*C*H), 129.5 (*C*H), 129.3 (*C*), 128.3 (*C*H), 123.5 (*C*H), 123.4 (*C*H), 123.1 (*C*H), 22.2 (*C*H_3), −0.8 (Si(*C*H_3)$_3$); MS (70 eV) *m*/*z* (%) 316 (M^+, 7), 302 (30), 301 (100).

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Supporting Information Available: Experimental procedures and characterization of all new compounds, copies of ^{1}H NMR and ^{13}C NMR for all new compounds, computational details and geometries for all computed structures, a table of absolute energies, $<S^2>$ expectation values, and a figure with the structures of **2a** and **6a** superimposed. This material is available free of charge via the Internet at http://pubs.acs.org.

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