On the Di-1-naphthylcarbene-Dibenzofluorene Rearrangement and the Ethylenization of Diarylcarbinols

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On the Di-1-naphthylcarbene−Dibenzofluorene Rearrangement and the Ethylenization of Diarylcarbinols

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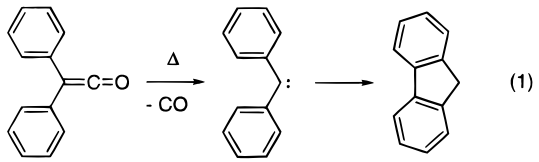
Solution-spray flash vacuum thermolysis of di-1-naphthyldiazomethane (**9**) results in the formation of dibenzo[*c*,*g*]fluorene (**12**), formed via a carbene−carbene rearrangement of di-1-naphthylcarbene (**10**). The isomeric dibenzo[*a*,*i*]fluorene (**11**) claimed by Franzen and Joschek (*Liebigs Ann. Chem.* **1960**, *633*, 7) is *not* formed, and no dibenzofluorene is formed on thermolysis in boiling naphthalene. **11** is formed on dehydration of di-1-naphthylcarbinol (**14**) with phosphoric acid, but the claimed tetra-1-naphthylethylene (**13**) is *not* formed, and the so-called ethylenization of diarylcarbinols is cast in doubt generally. The compound previously believed to be **13** is 13-[di(1-naphthyl)methyl]-dibenzo[*a*,*i*]fluorene (**22**). The alleged cleavage of **13** into two molecules of carbene **10** is unsubstantiated.

Introduction

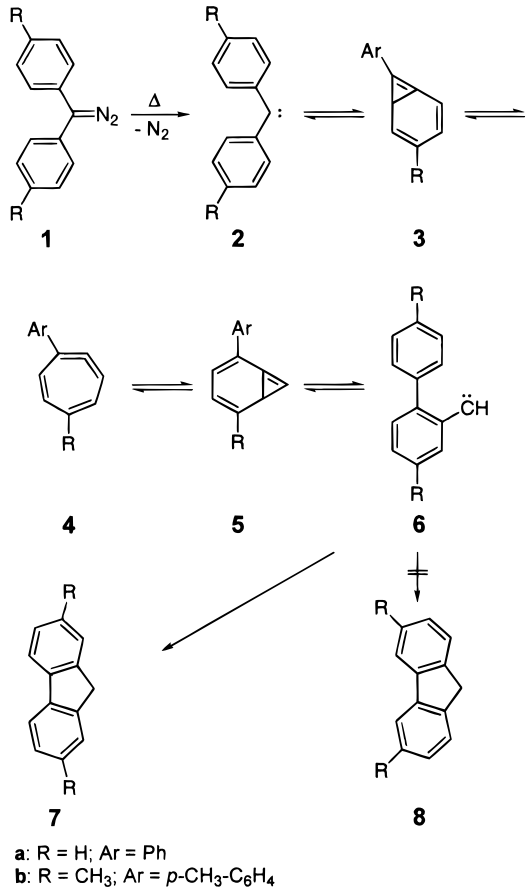
The rearrangement of diphenylcarbene to fluorene was first reported by Staudinger and Endle[1] as the result of pyrolysis of diphenylketene through a quartz tube at 600−700 °C in a water aspirator vacuum (eq 1). Al-



(1)

though it would be natural to assume that this reaction involved bond formation between C-2 and C-2′,[1] detailed investigations of substituted diphenylcarbenes (produced by thermolysis of diaryldiazomethanes) have clearly demonstrated that a deep-seated carbene−carbene rearrangement is in fact the exclusive path.[2] For example, flash vacuum thermolysis (FVT) of (*p*,*p*′-ditolyl)diazomethane (**1b**) gives 2,7-dimethylfluorene (**7b**) in high yield with no trace of the isomeric 3,6-dimethylfluorene (**8b**).[2a] This reaction was one of the earliest pieces of evidence for the aromatic carbene−carbene rearrangement, proceeding by ring expansion and ring contraction via the carbenes **2** and **6**, the cycloheptatetraene **4**, and possibly the (unobserved) bicycloheptatrienes **3** and **5** (Scheme 1).[3] Recent theoretical calculations on the phenylcarbene−bicycloheptatriene−cycloheptatetraene rearrangement reveal that the cycloheptatetraenes are likely to be global minima on the singlet energy surfaces, with the bicycloheptatrienes as shallow minima that will be difficult to detect experimentally, and the triplet carbenes as global minima on the triplet surfaces.[4]

Scheme 1



(1) Staudinger, H.; Endle, R. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 1437−1442. The reaction was also formulated in that way by Harrison and Lossing (Harrison, H. D.; Lossing, P. F. *J. Am. Chem. Soc.* **1960**, *82*, 1052) (using bromodiphenylmethane as a thermal precursor of diphenylcarbene and fluorene) and by Rice and Michaelsen (Rice, F. O.; Michaelsen, J. D. *J. Phys. Chem.* **1962**, *66*, 1535) (using diphenyldiazomethane as a thermal precursor).

(2) (a) Wentrup, C.; Wilczek, K. *Helv. Chim. Acta* **1970**, *53*, 1459−1463. (b) Myers, J. A.; Joines, R. C.; Jones, W. M. *J. Am. Chem. Soc.* **1970**, *92*, 4740−4742. (c) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173−251.

(3) For further reviews of carbene−carbene rearrangements, see also: Wentrup, C. *Reactive Molecules*; Wiley: New York, 1984. Jones, W. M. In *Rearrangements in Ground and Excited States*; de Mayo, P. Ed.; Academic: New York, 1980; Vol. 1, pp 95−161. Wentrup, C. In *Reactive Intermediates*, Abramovitch, R. A., Ed.; Plenum: New York, 1980; Vol. 1, pp 263−319.

(4) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535−1542. Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F. *J. Org. Chem.* **1996**, *61*, 7030−7039. Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022−7029.

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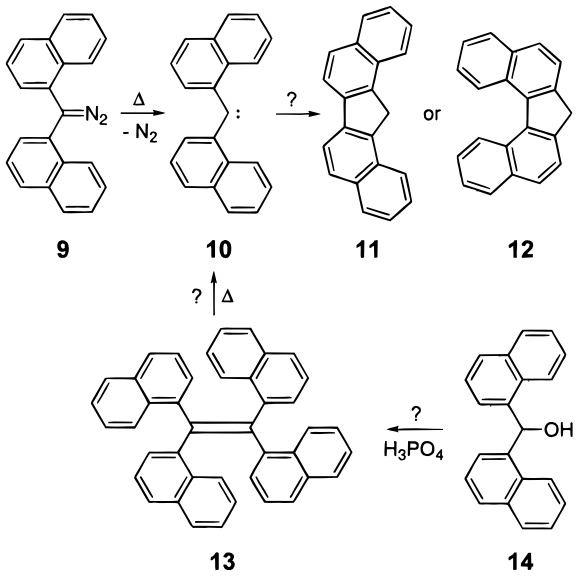
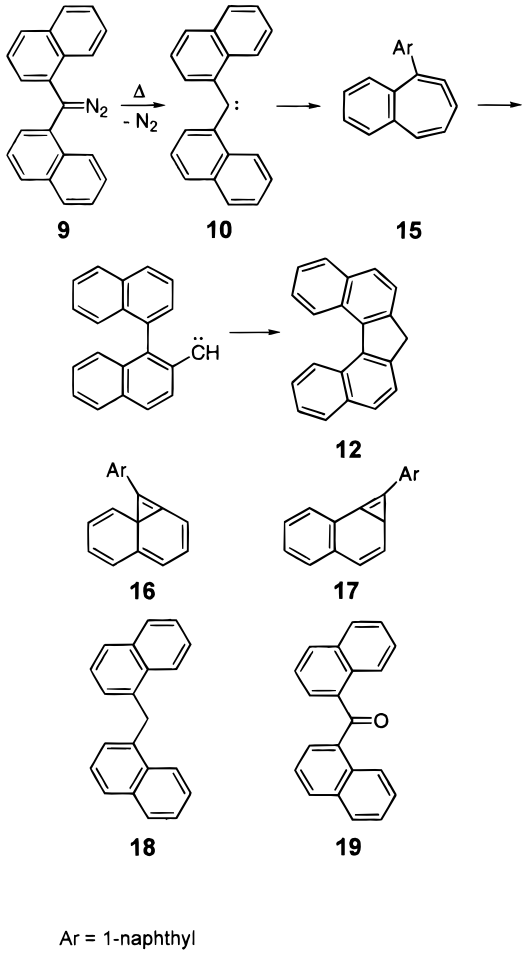
Scheme 2



Scheme 3



Calculations (B3LYP/6-311+G**//B3LYP/6-31G*+ZPVE) on the diphenylcarbene (**2a**) energy surface are in agreement with these general trends: the cycloheptatetraene **4a** is ca. 6 kcal/mol below singlet diphenylcarbene **2a**, the singlet 2-biphenylylcarbene **6a** is ca. 12 kcal/mol above **2a**, the bicycloheptatrienes **3a** and **5a** are ca. 6 and 10 kcal/mol above singlet **2a**, respectively, and the fluorene **7a** is ca. 75 kcal/mol below singlet **2a**, thus making the overall reaction strongly exothermic. The overall barrier height for the whole ring expansion−ring contraction−cyclization process from **2a** to **7a** is no more than ca. 23 kcal/mol at this level of theory.[5]

However, there is one report in the literature of the direct cyclization of a diarylcarbene to a fluorene, not involving a carbene−carbene rearrangement: in 1960, Franzen and Joschek reported two surprising observations[6] (both wrong, as we shall show). (i) Thermolysis of di-1-naphthyldiazomethane (**9**) in boiling naphthalene (219 °C) gave dibenzo[*a*,*i*]fluorene (**11**) (Scheme 2). (ii) The same dibenzo[*a*,*i*]fluorene (**11**) was also produced by thermal cleavage of tetra-1-naphthylethylene (**13**) into two carbenes **10**, followed by cyclization. Both the ethylene **13** and the dibenzofluorene **11** were synthesized according to a method previously described by Tschitschibabin and Magidson,[7] whereby di-1-naphthylcarbinol (**14**) is treated with phosphoric acid (Scheme 2). This "ethylenization" reaction, allegedly producing **13** in the present case, has been the subject of other investigations and stands unchallenged in the literature.[8]

In this paper, we demonstrate that not only are the conclusions of Franzen and Joschek[6] wrong; the premise that "ethylenization" of diarylcarbinols occurs on treatment with phosphoric acid is also erroneous. Tetra-1-naphthylethylene (**13**) is in fact *not* formed, and it is still an unknown compound. Dibenzo[*a*,*i*]fluorene (**11**) *is* formed in the Magidson reaction, but it is *not* formed in the Franzen−Joschek reaction, where the isomer **12** (dibenzo[*c*,*g*]fluorene) is formed instead.

Results and Discussion

To be able to identify the isomeric dibenzofluorenes **11** and **12** unambiguously, authentic samples were synthesized according to the method of Harvey et al.[9] The two fluorenes are distinguished by their melting points, ^{1}H and ^{13}C NMR spectra, and GC retention times, **12** eluting before **11**. Since di-1-naphthyldiazomethane (**9**) is too involatile for normal FVT, it was investigated by solution-spray flash vacuum thermolysis (SS-FVT)[10] of a benzene solution at 660 °C. GC−MS analysis of the volatile products allowed the identification of dibenzo[*c*,*g*]fluorene **12** (11−19%), di-1-naphthylmethane (**18**) (8−10%), and di-1-naphthyl ketone (**19**) (40−55% of the volatile fraction). Most importantly, only **12**, and none of the isomer **11**, was formed. This implies that the formation of **12** takes place via carbene−carbene rearrangement, according to Scheme 3. (Experiments reported below reveal that **11**, if formed, would have been perfectly stable under the SS-FVT conditions.) Note that, if a bicycloheptatriene intermediate is involved, this will be compound **16** rather than **17**. There are several examples of

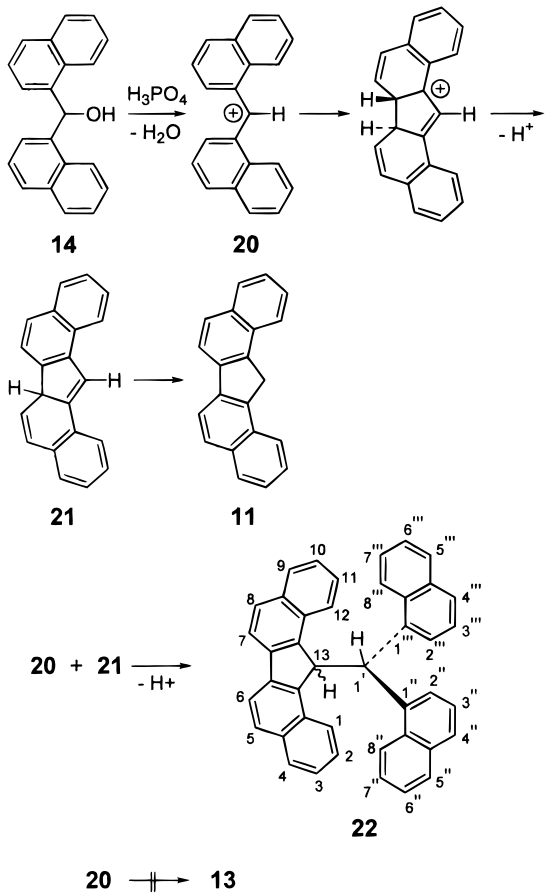
(5) Wong, M. W.; Wentrup, C. To be published.
(6) Franzen, V.; Joschek, H.-I. *Liebigs Ann. Chem.* **1960**, *633*, 7−13.
(7) (a) Tschitschibabin, A. E.; Magidson, O. I. *J. Prakt. Chem.* **1914**, *90*, 168−177. (b) Magidson, O. I. *Ber. Dtsch. Chem. Ges.* **1925**, *58*, 433−442.
(8) Bergmann, F.; Israelashvili, S. *J. Am. Chem. Soc.* **1946**, *68*, 354−356.
(9) Harvey, R. G.; Pataki, J.; Cortez, C.; Raddo, P. D.; Yang, C. X. *J. Org. Chem.* **1991**, *56*, 1210−1217.
(10) Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F.; *J. Am. Chem. Soc.* **1991**, *113*, 6943−6949.

arylcarbene or -nitrene ring expansion taking place in the direction of the ring junction, corresponding to **16** and **15**.[11]

Franzen and Joschek reported the formation of **11** when a benzene solution of the diazo compound **9** was added to boiling naphthalene. We repeated this experiment several times with negative results: no detectable amount of any dibenzofluorene was formed. Also, the use of diphenyl ether at 215 °C did not give any dibenzofluorene. In both cases, the only identifiable volatile products were di-1-naphthylmethane (**18**) and di-1-naphthyl ketone (**19**) (ca. 1:2). The observation of fluorene **12** as a product would have been important as a unique example of an aromatic carbene−carbene rearrangement in solution. In fact, no bona fide example of such a reaction is known.[12]

Next, Magidson's "tetra-α-naphthylethylene" synthesis was repeated.[7] The dehydration of di-1-naphthylcarbinol (**14**) with phosphoric acid produces the cation **20**, which cyclizes to an intermediate **21** before (inter- or intramolecular) hydrogen shifts to give dibenzo[*a*,*i*]fluorene **11** (Scheme 4).[13] Comparison with the authentic **11** proved that this product was correctly formulated by the original investigators,[7] but it is different from the dibenzofluorene **12** obtained in the carbene−carbene rearrangement (Scheme 3). The second product of this reaction was supposed to be **13**.[7] However, detailed ^{1}H and ^{13}C NMR investigations revealed that it is not at all an olefin. This, therefore, is also likely to be the case with other reported "ethylenization" reactions.[8,14] Instead, Magidson's second product is 13-[di(1-naphthyl)methyl]dibenzo[*a*,*i*]fluorene **22**. This product is obtained in 49% yield at 160 °C. The mechanism for its formation is described below (Scheme 4). The NMR spectra of **22** reveal 20 different aromatic carbons, of which seven are quarternary and two are aliphatic methine carbons, and 13 different protons integrating for 2H each and two additional protons integrating for 1H each. The extreme deshielding of the dinaphthyl methine proton in **22** (δ = 7.15 ppm) is particularly noteworthy. This is compared with related protons in similar compounds in Table 1, which demonstrates a progressive shift to lower fields as the number of aromatic rings around the methine proton increases. The methine protons of the fluorene moieties in **22** and in bis(dibenzo[*a*,*i*]fluorenyl) (**23**) are similarly affected, but to a smaller extent (5.9 ppm). DEPT and 2D spectra clearly showed that the low-field methine proton at 7.15 ppm correlates with an aliphatic CH carbon at 45.1 ppm, and homonuclear decoupling experiments (in CD_2Cl_2 and nitrobenzene-d_5) verified the coupling between the two

Scheme 4



methine protons at 7.15 and 5.9 ppm (J = 4.6 Hz). All the proton and carbon signals were assigned by means of selective decoupling and 2D correlation spectra. All the relevant spectra are reported in the Supporting Information.

Structure **22** can be described as having a di(1-naphthyl)methyl (DNM) moiety and a dibenzo[*a*,*i*]fluorenyl (DBF) moiety. In turn, the DBF moiety contains one two-spin and one four-spin system, whereas the DNM moiety has one three-spin and one four-spin system. There is one other two-spin system, that of the two aliphatic protons, H-1′ and H-13.

A 2D homonuclear ^{1}H−^{1}H shift correlation COSY spectrum permitted the identification of the spin system of each multiplet. Long-range ^{1}H−^{1}H couplings were established from a long-range COSY experiment. The one-bond ^{1}H−^{13}C connectivities were determined from an HSQC experiment, and long-range ^{1}H−^{13}C correlations were established from an HMBC experiment optimized for 6 Hz. The combined analysis of the data obtained from these 2D experiments permitted the unambiguous assignment of all protons and carbons. In particular, the doublet at 5.9 ppm corresponds to the aliphatic H-13 due to the long-range connectivities it shows with doublets at 7.81 and 7.87 ppm, the two-spin system of the DBF moiety in **22**.

The doublet at 7.81 ppm was assigned as H-5,8 on the basis of the three-bond connectivities with C-4,9, C-12a, 13b, and C6a,6b as well as the five-bond epi coupling[15] with H-1,12 due to the favorable zigzag arrangement.

(11) Wentrup, C.; Thétaz, C.; Tagliaferri, E.; Lindner, H. J.; Kitschke, B.; Winter, H. W.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 566−567. Wentrup, C.; Winter, H.-W. *J. Am. Chem. Soc.* **1980**, *102*, 6159−6161. Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. J. *Tetrahedron* **1985**, *41*, 1601−1612.

(12) Rearrangement of cycloheptatetraenes to phenylcarbenes in solution, but not the reverse, is known: Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353−359.

(13) For cationic cyclizations to produce fluorenes and related compounds, see: (a) Barclay, L. R. C. In *Friedel−Crafts and Related Reactions*; Olah, G. A., Ed; Interscience Publishers: New York, 1964; Vol. II, Part 2, pp 785−977. (b) Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1988**, *110*, 1862−1870. Ohwada, T.; Suzuki, T.; Shudo, K. *J. Am. Chem. Soc.* **1998**, *120*, 4629−4637 and references therein. (c) For the related Scholl condensations, see: Balaban, A. T.; Nenitzescu, C. D. In *Friedel−Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience Publishers: New York, 1964; Vol. II, Part 2, pp 979−1047.

(14) At best, only traces of tetraarylethylenes are formed. The analogous reaction of diphenylcarbinol with hot phosphoric acid gave a trace (≤0.1%) of tetraphenylethylene, identifiable only by GC−MS.

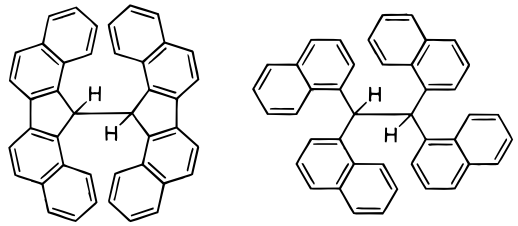
(15) Cho, B. P.; Harvey, R. G. *J. Org. Chem.* **1987**, *52*, 5679−5684.

Table 1. ^{1}H NMR Chemical Shifts of Aliphatic Protons

compd	(δ^1H)[a]
1-methylnaphthalene	2.7 (CH_3)
di(1-naphthyl)methane (**18**)	4.9 (CH_2)
diphenylmethane	3.9 (CH_2)
fluorene	3.8 (CH_2)
dibenzo[*c*,*g*]fluorene (**12**)	4.1 (CH_2)
dibenzo[*a*,*i*]fluorene (**11**)	4.5 (CH_2)
13,13′-bis(dibenzo[*a*,*i*]fluorenyl) (**23**)	5.9 (H(C-13))
tetra(1-naphthyl)ethane (**24**)	6.6 (H(C-1))
13-[di(1-naphthyl)methyl]dibenzo[*a*,*i*]fluorene (**22**)	5.9 (dibenzofluorenyl, H(C-13));[b] 7.1 (dinaphthylmethyl, H(C-1′))[b]

[a] Chemical shift in ppm relative to internal TMS; $CDCl_3$ solutions. [b] For the numbering of compound **22**, see Scheme 4.

Chart 1



23 **24**

Similarly, in the DNM moiety, the doublet at 7.59 ppm was assigned as H-4″,4‴ due to its three-bond connectivities with C-2″,2‴, C-5″,5‴, and C-8a″,8a‴ as well as an epi coupling to H-8″,8‴.

The ^{1}H and ^{13}C NMR spectra of bis(dibenzo[*a*,*i*]fluorenyl) (**23**) are also interesting: at room temperature, only broad, unresolved signals are observed in the aromatic C−H regions, presumably due to slow rotation of the two fluorenyl moieties. At 131 °C ($CDCl_2CDCl_2$ solution), the faster rotation results in well-resolved spectra. The spectra are shown in the Supporting Information.

A mechanism for the formation of **22** involves a coupling between the dinaphthylmethyl cation **20** and the intermediate **21** (Scheme 4). We found that **22** was also produced, albeit in only 5% yield, on treatment of carbinol **14** with trifluoromethanesulfonic acid at −40 to +18 °C. From this and other experiments, it can be concluded that the reaction of the dinaphthylmethyl cation **20** to give **22** occurs over a temperature range from −40 to +200 °C. Note that, in experiments reported by Ohwada et al.,[13b] a different type of diphenylmethylfluorene (substituted in the six-membered rings, not on the fluorene-CH_2 group, by one or two diphenylmethyl groups) was obtained on treatment of certain diphenylcarbinols with TFSA.

Having established that this "Magidson compound" (**22**) is not an ethylene, the claimed cleavage of "tetra-1-naphthylethylene" into two carbenes[6] is of course erroneous. Franzen and Joschek did obtain dibenzo[*a*,*i*]-fluorene (**11**) by thermolysis of **22**, not surprisingly since this moiety is contained in **22**, but it was not formed via any carbene reaction. We checked the thermolysis of compound **22** in boiling naphthalene (Franzen−Joschek conditions) and also by SS-FVT and confirmed that dibenzo[*a*,*i*]fluorene (**11**) is in fact formed in this case. In the naphthalene melt, 5% of **11** was obtained, together with di-1-naphthylmethane (**18**) (<1%), tetra-1-naphthylethane (**24**) (47%), and bis(dibenzo[*a*,*i*]fluorenyl) (**23**) (42%) (Chart 1); these are assumed to be cleavage/recombination products. In the SS-FVT experiment, 58% of **11**, 24% of **18**, and 4% of **23** were obtained. Compound **22** is also cleaved on treatment with hot phosphoric acid, affording a mixture of di-1-naphthylmethane (**18**) and dibenzo[*a*,*i*]fluorene (**11**), together with the recombination products **23**, **24**, and recovered **22**. Under the conditions of the Scholl reaction[13c] ($AlCl_3$ in benzene), **22** did not undergo dehydrogenating condensation to give bis(dibenzofluorenyl) **23** but instead afforded dibenzo[*a*,*i*]fluorene (**11**) in 35% yield.

Conclusion

Di-1-naphthylcarbene (**10**) rearranges to dibenzo[*c*,*g*]-fluorene (**12**) under the conditions of solution-spray flash vacuum thermolysis. The isomeric dibenzo[*a*,*i*]fluorene (**11**) is not formed. No dibenzofluorene is formed on thermolysis of di-1-naphthyldiazomethane (**9**) in boiling naphthalene.

The "ethylenization" of diarylcarbinols, in particular the formation of tetra-1-naphthylethylene (**13**) on treatment of di-1-naphthylcarbinol (**14**) with phosphoric acid,[6−8] is shown to be mistaken. The products formed are dibenzo[*a*,*i*]fluorene (**11**) and 13-[di(1-naphthyl)methyl]-dibenzo[*a*,*i*]fluorene **22**. Tetra-1-naphthylethylene is an unknown compound, and its alleged cleavage[6] into two carbenes (**10**) on thermolysis was mistaken.

Experimental Section

General Methods. 1D and 2D NMR spectra were recorded on a Bruker AMX400 spectrometer at 28 °C, observing ^{1}H and ^{13}C at 400.13 and 100.62 MHz, respectively, unless otherwise stated. The ^{1}H and ^{13}C chemical shifts are reported in ppm from TMS (δ scale) but were measured against the $CDCl_3$ ($CHCl_3$) solvent peaks at 7.24 and 77.00 ppm, respectively, unless otherwise stated.

Phase-sensitive 2D spectra were obtained using phase-proportional time incrementation. DQF-COSY[16] spectra were acquired over a spectral width of 1445 Hz (**22**) or 2049 Hz (**11**) using 16 scans, a recycle time of 3.5 s, and 2048 data points. Either 512 (**22**) or 963 (**11**) increments in F1 were collected. The 60° phase shifted sine bell squared window functions were applied in both dimensions before transformation of the matrix, which was zero filled in F1 to either 512 (**22**) or 1024 (**11**) points. A magnitude mode COSY spectrum was obtained for **22** with a delay of 0.2 s to optimize long-range couplings[17] using the same acquisition parameters as for the DQF-COSY spectrum.

An ^{1}H−^{13}C HSQC[18] spectrum was accumulated for **22** over a proton spectral width of 1445 Hz and a C-13 spectral width of 9090 Hz using 24 scans, a recycle time of 2.1 s, and 512

(16) Derome, A. E.; Williamson, M. P. *J. Magn. Reson.* **1990**, *88*, 177−185.
(17) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542−561.
(18) Bodenhausen, G.; Ruben, D. J. *Chem. Phys. Lett.* **1980**, *69*, 185−189.

data points in F2. C-13 decoupling was applied during acquisition. A total of 987 increments in F1 were applied, 90° phase-shifted sine bell squared window functions were applied in both dimensions before transformation, and the matrix was zero filled to 512 points in F2 and 1024 points in F1. An $^1H-^{13}C$ HMBC[19] magnitude mode experiment was obtained for **22** using conditions as for the HSQC except that the C-13 spectral width was 11 900 Hz and 64 scans were acquired for each of the 1024 increments in F1. The delay for evolution of long-range couplings was optimized for $J = 6$ Hz (83 ms).

GC−MS analyses were made on a Hewlett-Packard quadrupole mass-selective detector 5970 connected to a gas chromatograph equipped with a BP-5 capillary column (30 m × 0.25 mm with 0.25 m phase thickness; He carrier at 20 psi head pressure; injector, 200 °C; detector 280 °C; column temperature, 100−250 °C, programmed at 16 °C/min). Identification of known compounds by ^1H NMR and GC−MS analysis of mixtures was done by direct comparison with authentic samples. Melting points are uncorrected. Column chromatography was performed using neutral Al_2O_3 (activity I) unless otherwise stated. Di(1-naphthyl) ketone (**19**)[20] and di(1-naphthyl)carbinol[20] (**14**) were synthesized according to literature procedures.

Di(1-naphthyl) Ketone Hydrazone. Standard procedures[21] for hydrazone preparation were modified as follows. Di(1-naphthyl) ketone[20] (**19**) (0.20 g, 0.71 mmol) was dissolved in 5 mL of dry *n*-butanol; 1.0 mL of anhydrous hydrazine was added to the solution, which was then refluxed under N_2. After both the second and the third day of reflux, 1.5 g of anhyd $MgSO_4$ and 0.5 mL of anhyd hydrazine were added to the mixture. According to GC−MS analysis, complete conversion to the hydrazone was achieved after 6 d of reflux. The hot solution was filtered to remove $MgSO_4$, and the solid was washed with hot ethanol. After concentration and cooling, 0.15 g (71%) of the hydrazone was obtained: mp 147−149 °C (lit.[6] mp 148 °C); ^1H NMR (200 MHz) δ 8.9 (d, $J = 6.8$ Hz, 1 H), 7.8−7.9 (m, 4 H), 7.7 (dd, $J = 7.5$, 1.6 Hz, 1 H), 7.4−7.6 (m, 6 H), 7.2−7.3 (m, 2 H), 5.3 (s, 2 H); ^{13}C NMR (50 MHz) δ 148.7 (s), 135.6 (s), 134.3 (s), 133.8 (s), 132.4 (s), 131.1 (s), 129.9 (s), 129.5 (d), 128.9 (d), 128.7 (d), 128.4 (d), 127.8 (d), 127.3 (d), 127.1 (d), 126.7 (d), 126.6 (d), 126.4 (d), 125.9 (d), 125.8 (d), 125.4 (d), 124.8 (d).

Di(1-naphthyl)diazomethane (9). To a solution of 0.18 g (0.61 mmol) of di(1-naphthyl) ketone hydrazone in 10 mL of dry ether were added 0.30 g of anhyd Na_2SO_4, 0.5 mL of a saturated ethanolic potassium hydroxyde solution, and 0.90 g of yellow HgO. The flask was cooled in an ice bath, and the mixture was stirred in the dark for 10 h. After filtration, the solvent was removed on a rotary evaporator, and the bright red residue was dissolved in hexane. Upon cooling, 0.17 g (95%) of **9** was obtained as red crystals: mp 75−80 °C dec (lit.[22] mp 75 °C dec); ^1H NMR δ 7.88−7.92 (m, 4 H), 7.80 (d, $J = 8.2$ Hz, 2 H), 7.50 (ddd, $J = 8.2$, 6.9, 1.2 Hz, 2 H), 7.44 (t, $J_A = J_B = 7.7$ Hz, 2H), 7.41 (ddd, $J = 8.4$, 6.9, 1.4 Hz, 2 H), 7.37 (dd, $J = 7.2$, 1.2 Hz, 2 H); ^{13}C NMR δ 134.5 (s), 130.6 (s), 128.9 (d), 128.7 (s), 127.8 (d), 126.4 (d), 126.3 (d), 126.1 (d), 125.8 (d), 124.8 (d), 58.3 (s).

Dibenzo[*c,g*]fluorene (12):[9] mp 141−143 °C (lit.[9] mp 142.5−143 °C); ^1H NMR δ 8.76 (dd, $J = 8.4$, 0.6 Hz, 2H), 7.99 (dd, $J = 8.0$, 1.6 Hz, 2H), 7.87 (d, $J = 8.1$ Hz, 2H), 7.73 (d, $J = 8.1$, 2H), 7.5−7.6 (m, 4H), 4.11 (s, 2H); ^{13}C NMR δ 142.9 (s), 138.3 (s), 133.9 (s), 128.8 (s), 128.7 (d), 127.7 (d), 126.7 (d), 124.8 (d), 124.7 (d), 122.8 (d), 38.9 (t); GC−MS retention time 21.7 min.

Dibenzo[*a,i*]fluorene (11):[9] mp 232−233 °C (lit.[9] mp 231−233 °C); ^1H NMR δ 8.12 (d, $J = 8.3$ Hz, 2H, H1,12), 7.98 (d, $J = 8.3$, 2H, H6,7), 7.90−7.94 (m, 4H, H4,5,8,9), 7.57 (ddd, $J = 8.2$, 6.9, 1.1, 2H, H2,11), 7.47 (ddd, $J = 8.1$, 6.9, 1.2, 2H, H3, 10) 4.47 (s, 2H, H13,13′) (assignments are based on 2D homonuclear $^1H-^1H$ coupling (COSY) experiments and differ from those given in ref 9; in particular, an epi coupling[15] between H-5,8 and H-1,12 was observed, which allowed the assignment of the rest of the proton signals. The 2D spectrum is shown in the Supporting Information); ^{13}C NMR δ 139.9 (s), 139.8 (s), 132.7 (s), 130.7 (s), 129.0 (d), 127.8 (d), 126.5 (d), 125.2 (d), 124.0 (d), 118.7 (d), 34.4 (t); GC−MS retention time 23.6 min.

Tetra(1-naphthyl)ethane (24) was prepared according to the literature[23] from di(1-naphthyl)chloromethane in 93% yield: mp 282−285 °C (lit.[20a] mp 285−286 °C); ^1H NMR δ 7.94 (d, $J = 8.4$ Hz, 4 H) 7.59 (d, $J = 7.2$ Hz, 4 H), 7.54 (d, $J = 8.0$ Hz, 4 H), 7.44 (d, $J = 8.1$ Hz, 4 H) 7.09−7.21 (m, 12 H), 6.65 (s, 2 H); ^{13}C NMR δ 139.5 (s), 133.5 (s), 131.8 (s), 128.33 (d), 128.28 (d), 127.1 (d), 126.8 (d), 125.5 (d), 124.9 (d), 124.7 (d), 123.0 (d), 45.9 (d).

13,13′-Bis(dibenzo[*a,i*]fluorenyl) (23). A mixture of dibenzo[*a,i*]fluorene (**11**) (0.136 g, 0.511 mmol) and dibenzoyl peroxide (0.078 g, 0.32 mmol) was refluxed in 15 mL of dry benzene for 2.5 d. More dibenzoyl peroxide (0.075 g, 0.31 mmol) was added, and the mixture was refluxed for another 2.5 d. The solvent was removed to give a brown residue, which was washed with a small amount of acetone. The off-white solid was then dissolved in a minimum amount of boiling benzene. The fine white solid that separated upon cooling was recovered by filtration. This afforded 44 mg (32%) of **23**: mp upon fast heating in an open capillary: the solid turned brown at 320−325 °C and melted at 340−341 °C (lit.[7b] mp 338−350 °C, lit.[24] mp 353−355 °C); ^1H NMR ($CDCl_3$, 27 °C) δ 7.0−8.2 (unresolved broad band) 5.88 (s); ^1H NMR ($CDCl_2CDCl_2$, 131 °C) δ 7.83 (d, $J = 8.3$ Hz, 4 H), 7.69 (d, $J = 8.3$ Hz, 4 H), 7.3−7.4 (br m, 12 H), 7.23 (br t, 4 H), 5.94 (s, 2 H); ^{13}C NMR ($CDCl_3$, 27 °C) δ 141.6, 130.4, 123−125 (br signal), 51.6; ^{13}C NMR ($CDCl_2CDCl_2$, 131 °C) δ 141.9, 140.2, 133.3, 130.8, 129.0, 128.6, 125.8, 124.6, 124.3, 118.1, 52.0.

Reaction of Di(1-naphthyl)carbinol (14) with Anhydrous Phosphoric Acid. This reaction[6,7] was performed as follows.

(a) A 0.50 g (1.8 mmol) portion of the carbinol **14** and 1.5 g of crystalline H_3PO_4 were ground together. The paste was transferred to a round-bottomed flask, which was evacuated at 1−2 mbar. The flask was placed in an oil bath at 160 °C for 1 h. The resulting solid was crushed to a powder, washed with distilled H_2O, and taken up in benzene. The organic phase was washed with H_2O until the water washings were neutral. The benzene phase was dried with anhyd $MgSO_4$ and then concentrated to give 0.45 g of crude reaction mixture. Column chromatography (hexane−benzene 10:1, changed gradually to 1:1) afforded the following compounds:

Di(1-naphthyl)methane (**18**) as the first fraction: 0.02 g (4%) of as white needles: mp 108−109 °C (lit.[20b] mp 107−108 °C); ^1H NMR (200 MHz) δ 8.0 (m, 2 H), 7.9 (m, 2 H), 7.8 (d, $J = 8.2$ Hz, 2 H), 7.5 (m, 4 H), 7.4 (dd, $J = 8.1$, 7.1 Hz, 2 H), 7.1 (d, $J = 7.0$ Hz, 2 H), 4.9 (s, 2H); ^{13}C NMR (50 MHz) δ 136.1 (s), 133.8 (s), 132.2 (s), 128.7 (d), 127.1 (d), 127.0 (d), 126.1 (d), 125.6 (d), 125.6 (d), 123.9 (d), 35.7 (t).

Dibenzo[*a,i*]fluorene (**11**) as the second fraction: 0.16 g (34%) of as white platelets; mp 233−234 °C; identified by NMR and GC−MS comparison with the sample described above.

13*H*-13-[Di(1-naphthyl)methyl]dibenzo[*a,i*]fluorene (22) as the third fraction: 0.23 g (49%); mp > 260 °C dec in open capillary with fast heating; ^1H NMR (CD_2Cl_2) δ 8.09 (d, $J = 8.4$ Hz, 2 H, H8″,8‴), 7.87 (d, $J = 8.3$ Hz, 2 H, H6,7), 7.81 (d, $J = 8.4$ Hz, 2 H, H5,8), 7.75−7.78 (m, 4 H, H4,9,5″,5‴), 7.59 (d, $J = 8.2$ Hz, 2 H, H4″,4‴), 7.55 (d, $J = 8.5$ Hz, 2 H, H1,12), 7.38 (ddd, $J = 8.0$, 6.8, 1.2 Hz, 2 H, H6″,H6‴), 7.33 (ddd, $J = 8.4$, 6.8, 1.6 Hz, 2 H, H7″,H7‴), 7.26 (ddd, $J = 8.1$, 6.8, 1.2 Hz, 2 H, H3,10), 7.08−7.15 (m, 5 H, H1′,2,11,2″,2‴), 7.01 (t,

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$J_A = J_B = 7.7$ Hz, 2 H, H3″,H3‴), 5.99 (d, $J = 4.6$ Hz, 1 H, H13); ^{13}C NMR (CD2Cl2) δ 144.1 (s, C12b,13a) 141.0 (s, C6a, 6b), 137.9 (s, C1″,1‴), 134.4 (s, C4a″,4a‴), 133.5 (s, C4a,8a), 132.5 (s, C8a″,8a‴), 130.8 (s, C12a,13b), 129.2 (d, C5″,5‴), 129.1 (d, C4,9), 129.0 (d, C5,8), 127.7 (d, C4″,4‴), 127.4 (d, C2″,2‴), 126.4 (d, C7″,7‴), 126.0 (d, C2,11), 125.7 (d, C6″,6‴), 125.5 (d, C1,12), 125.2 (d, C3″,3‴), 125.0 (d, C3,10), 123.5 (d, C8″,8‴), 118.5 (d, C6,7), 51.6 (d, C13), 45.1 (d, C1′). Anal. Calcd for $C_{42}H_{28}$: C, 94.70; H, 5.30. Found: C, 94.61; H, 5.25.

In addition, a fraction was collected that contained a mixture of **22** and 13,13′-bis(dibenzo[*a*,*i*]fluorenyl) (**23**) (<10 mg), identified by ^{1}H NMR comparison with the above sample.

(b) A 1.00 g portion of **14** and 3.5 g of crystalline H_3PO_4 were ground together. The paste was heated at 200 °C in a vacuum (1−2 mbar) for 2 h. The usual workup afforded 0.66 g of a beige solid. ^{1}H NMR analysis revealed a mixture of di(1-naphthyl)methane (**18**) (24%), dibenzo[*a*,*i*]fluorene (**11**) (66%), 13,13′-bis(dibenzo[*a*,*i*]fluorenyl) (**23**) (7%), and a trace of **22** (3%).

Reaction of Di(1-naphthyl)carbinol (14) with TFSA. To 4.5 mL of TFSA cooled to −40 °C in a dry ice−ethanol bath was added 0.16 g (0.56 mmol) of di(1-naphthyl)carbinol in portions with vigorous stirring. The system was maintained under N_2, and a dark blue solution formed upon addition of the carbinol. The solution was warmed slowly to 18 °C in the course of 3−4 h before the usual aqueous workup. ^{1}H NMR analysis of the product mixture (beige solid, 0.12 g) revealed that mostly starting material was recovered (80%) with some bis[di(1-naphthyl)methyl] ether (10%), **22** (5%), **11** (2%), and **18** (1%).

Bis[di(1-naphthyl)methyl] ether was prepared for comparison by dehydration of di(1-naphthyl)carbinol (**14**) with HCl at 150 °C/0.5 mbar:[7a] mp 248−250 °C (lit.[7a] mp 246.5 °C); ^{1}H NMR (200 MHz) δ 7.80−7.86 (m, 8 H), 7.72 (d, $J = 6.7$ Hz, 4 H), 7.31−7.45 (m, 12 H), 7.15 (s, 2 H), 7.01 (ddd, $J = 8.4$, 7.0, 1.3 Hz, 4 H); ^{13}C NMR (50 MHz) δ 136.9 (s), 133.7 (s), 131.5 (s), 128.7 (d), 128.4 (d), 126.4 (d), 126.1 (d), 125.5 (d), 125.4 (d), 123.4 (d), 73.2 (d).

Reaction of 13*H*-13-[Di(1-naphthyl)methyl]dibenzo[*a*,*i*]fluorene (22) with Anhyd H_3PO_4. A 0.25 g (0.47 mmol) portion of **22** and 2.3 g of crystalline H_3PO_4 were ground together. The paste was heated at 240 °C under N_2 for 2.5 h. After cooling, the brown mixture was dissolved in benzene and washed three times with a saturated $NaHCO_3$ solution and then three times with distilled H_2O. The benzene phase was dried with anhyd $MgSO_4$ and then concentrated to give 0.21 g of the crude product mixture. Column chromatography (hexane−benzene 1:0, changed gradually to 1:1) afforded 0.02 g (8%) of di(1-naphthyl)methane (**18**), 0.06 g (24%) of dibenzo[*a*,*i*]fluorene (**11**), and 0.08 g of a mixture that, analyzed by ^{1}H NMR, revealed the presence of tetra(1-naphthyl)ethane (**24**) (3%), 13*H*-13-[di(1-naphthyl)methyl]dibenzo[*a*,*i*]fluorene (**22**) (3%), 13,13′-bis(dibenzo[*a*,*i*]fluorenyl) (**23**) (15%), and an unknown exhibiting singlets at 4.6, 7.4, and 7.6 ppm in a ratio of 2:1:1 (possibly an isomeric (dinaphthylmethyl)dibenzofluorene of the Ohwada type[13b] (ca. 9%)).

Reaction of 13*H*-13-[Di(1-naphthyl)methyl]dibenzo[*a*,*i*]fluorene (22) with $AlCl_3$. A 0.05 g (0.094 mmol) portion of **22** was stirred in 30 mL of dry benzene with 0.06 g (0.45 mmol) of $AlCl_3$ at room temperature for 4 h. TLC of the mixture indicated the formation of dibenzo[*a*,*i*]fluorene (**11**) and that starting material was still present. The mixture was refluxed overnight, after which time TLC indicated that all starting material had been consumed. The benzene phase was washed with H_2O, dried with anhyd $MgSO_4$, and then concentrated to give 0.04 g of a red/brown solid. ^{1}H NMR and GC−MS analysis revealed a mixture of dibenzo[*a*,*i*]fluorene (**11**) (35%), triphenylmethane (35%), diphenylmethane (15%), and naphthalene (10%). A similar experiment with $AlCl_3$ in refluxing CS_2 afforded a 22% yield of **11**.

Thermolysis of 13*H*-13-[Di(1-naphthyl)methyl]dibenzo[*a*,*i*]fluorene (22) in Naphthalene. A mixture of 50.0 mg (0.094 mmol) of **22** and 3.0 g of naphthalene was heated until the naphthalene had melted and purged with N_2 for 30 min. The mixture was then refluxed at ca. 219 °C for 30 min, and the naphthalene was removed by sublimation. ^{1}H NMR analysis of the residue (beige solid, 47.2 mg) revealed a mixture of tetra(1-naphthyl)ethane (**24**) (47%), bis(dibenzo[*a*,*i*]fluorenyl) (**23**) (42%), recovered starting material (**22**) (5%), dibenzo[*a*,*i*]fluorene (**11**) (5%), and di(1-naphthyl)methane (**18**) (<1%).

Thermolysis of Di(1-naphthyl)diazomethane (9) in Naphthalene. A 9.2 mg portion of **9** was dissolved in 30 mL of dry benzene. The solution was protected from light and degassed using four freeze−pump−thaw cycles. Using a dry gastight syringe, the diazo solution was added dropwise to 10.0 g of refluxing naphthalene with vigorous stirring. Prior to the addition, the molten naphthalene had been purged with N_2 for 1 h. During the addition, the benzene was distilled off under a constant flow of N_2. Once the addition was complete, the naphthalene was carefully sublimed at 100 °C/1−2 mbar, leaving a dark yellow residue. No dibenzofluorene was detected either by ^{1}H NMR or by GC−MS analysis. Di(1-naphthyl)methane (**18**) and di(1-naphthyl) ketone (**19**) were the two major volatile products, obtained in a ratio of 1:2 according to the relative peak areas in the GC trace.

Thermolysis of Di(1-naphthyl)diazomethane (9) in Diphenyl Ether. A 9.5 mg portion of **9** was dissolved in 30 mL of freshly distilled phenyl ether. This solution was protected from light and purged with dry N_2 for 45 min. Using a dry gastight syringe, the diazo solution was added dropwise and with vigorous stirring to 30 mL of diphenyl ether (freshly distilled and purged with dry N_2 for 45 min) at 215 °C. The addition lasted 30 min, during which time the temperature dropped gradually to 200 °C. Most of the diphenyl ether was removed by vacuum distillation and the rest by Kugelrohr distillation, leaving a brown residue (20.9 mg). Column chromatography (hexane−benzene 9:1) afforded 11.7 mg of a yellow residue. No dibenzofluorene was detected by either ^{1}H NMR or GC−MS analysis of the product mixture. Again, di(1-naphthyl)methane (**18**) and di(1-naphthyl) ketone (**19**) were the two major volatile products, obtained in a ratio of 1:2.

Solution-Spray Flash Vacuum Thermolysis Method (SS-FVT). The general procedure described in the literature[10] was followed with some modifications. An electrically heated quartz pyrolysis tube (30 × 1.8 cm i.d.) was filled with quartz chips; a U-tube cooled in liquid N_2 was used to trap the products of the thermolysis; the thermolysis apparatus was evacuated by means of a turbomolecular pump (ca. 10^{-5} mbar); a metal tubing 0.9 m in length and of 0.4 mm o.d. was used instead of a Teflon needle; one end of this metal tubing was placed in the sample reservoir; the other was connected through a rubber septum (previously bleached in benzene) to a fine glass capillary inserted into the end of the pyrolysis tube. The metal tubing and capillary were purged with N_2 while being heated with a heat gun before use. A needle valve was used to control the flow of N_2 gas entering the sample reservoir (protected from light) containing a solution of the compound to be thermolyzed. This solution was degassed using three to four freeze−pump−thaw cycles. After thermolysis, the oven was cooled, and the frozen benzene solution in the U-tube was allowed to thaw under N_2. After concentration, the mixture of products was analyzed by GC−MS and ^{1}H NMR.

SS-FVT of Di(1-naphthyl)diazomethane (9). A degassed solution of 11.5 mg (0.0391 mmol) of **9** in 10−15 mL of dry benzene was thermolyzed at a temperature of 660 °C over the course of 30 min. GC−MS analysis of the mixture revealed the formation of di(1-naphthyl) ketone (**19**) (55%), dibenzo[*c*,*g*]fluorene (**12**) (19%) and di(1-naphthyl)methane (**18**) (8%). Similar results were obtained in repeat experiments.

SS-FVT of 13*H*-13-[Di(1-naphthyl)methyl]dibenzo[*a*,*i*]fluorene (22). A degassed solution of 12.0 mg (0.0226 mmol) of **22** in 15 mL of dry benzene was thermolyzed at 800 °C over 35 min. ^{1}H NMR of the product mixture revealed that dibenzo[*a*,*i*]fluorene (**11**) (58%) and di(1-naphthyl)methane (**18**) (24%) were the two major products. Some starting material (**22**) (14%) was recovered as well. A small amount of 13,13′-bis(dibenzo[*a*,*i*]fluorenyl) (**23**) (4%) was also observed. No diben-

zo[*c*,*g*]fluorene (**12**) or di(1-naphthyl) ketone (**13**) were detected by GC−MS or ^{1}H NMR analysis of the mixture.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra, selective ^{1}H decoupling experiments, DEPT-90 spectrum, 2D ^{1}H−^{1}H DQF-COSY, long-range ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, and long-range ^{1}H−^{13}C HMBC correlation spectra of **22**. ^{1}H NMR and ^{1}H−^{1}H DQF-COSY spectra of **11**. ^{1}H and ^{13}C NMR spectra of **23** at room temperature and at 131 °C (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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