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Scholl Cyclizations of Aryl Naphthalenes: Rearrangement Precedes Cyclization

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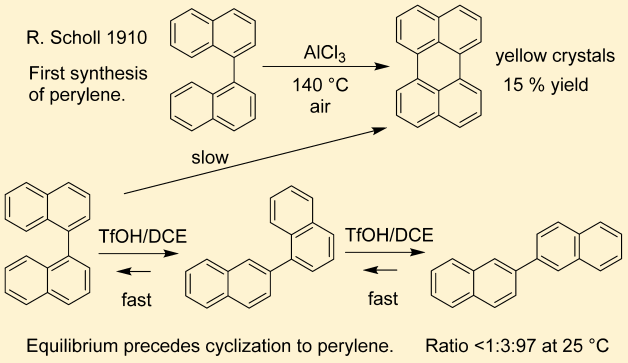
Supporting Information

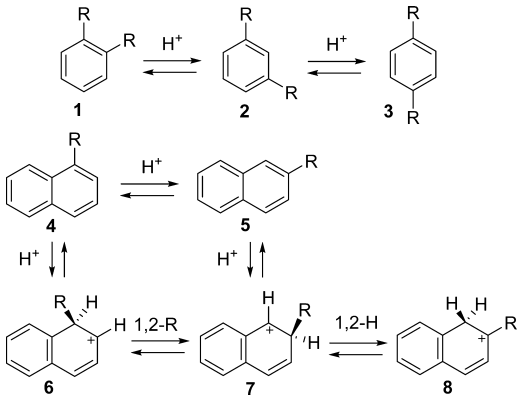
ABSTRACT: In 1910, Scholl, Seer, and Weitzenbock reported the $AlCl_3$-catalyzed cyclization of 1,1′-binaphthyl to perylene. We provide evidence that this classic organic name reaction proceeds through sequential and reversible formation of 1,2′- and 2,2′-binaphthyl isomers. Acid-catalyzed isomerization of 1,1′-binaphthyl to 2,2′-binaphthyl has been noted previously. The superacid trifluoromethanesulfonic acid (TfOH), 1 M in dichloroethane, catalyzes these rearrangements, with slower cyclization to perylene. Minor cyclization products are benzo[*k*]fluoranthene and benzo[*j*]fluoranthene. At ambient temperature, the observed equilibrium ratio of 1,1′-binaphthyl, 1,2′-binaphthyl, and 2,2′-binaphthyl is <1:3:97. DFT calculations with the inclusion of solvation support a mechanistic scheme in which *ipso*-arenium ions are responsible for rearrangements; however, we cannot distinguish between arenium ion and radical cation mechanisms for the cyclization steps. Under similar reaction conditions, 1-phenylnaphthalene interconverts with 2-phenylnaphthalene, with the latter favored at equilibrium (5:95 ratio), and also converts slowly to fluoranthene. Computations again support an arenium ion mechanism for rearrangements.



INTRODUCTION

It has long been known that alkyl-substituted[1] and aryl-substituted[2] benzenes (**1**−**3**) can interconvert (Scheme 1) in the presence of acid catalysts or reagents, such as aluminum chloride ($AlCl_3$), which generate a protic acid through reaction with adventitious water.[3] We recently studied the rearrangements of phenyl-substituted benzene derivatives through catalysis by 1 M trifluoromethanesulfonic acid (TfOH) in 1,2-dichloroethane (DCE).[4] This superacid[5] medium provides a more reliable and predictable alternative to $AlCl_3$. These rearrangements are believed to proceed by the formation of an *ipso*-arenium ion,[6] followed by a 1,2-shift of the substituent. With disubstituted benzenes, equilibrium favors *meta* substitution (**2**), a consequence of greater cationic product stability.

Scheme 1. Acid-Catalyzed Rearrangements



Much less studied have been similar rearrangements of substituted naphthalenes, which interconvert isomers **4** (alpha) and **5** (beta), presumably through *ipso* cations **6** and **7**. On this potential energy surface, the lowest-energy cation **8** is accessible by an additional 1,2-H shift in cation **7**; this is consistent with the preference for beta product described in the modest number of known examples. In 1976, Olah reported that alkyl naphthalenes isomerize during Friedel−Crafts alkylation, showing that substitution in the beta position was favored at equilibrium.[7] 1,2-Aryl migration catalyzed by BCl_3 has been reported in a congested 5,6-diaryl-substituted acenaphthene.[8] Kovacic and Koch first described the rearrangement (Scheme 2) of 1,1′-binaphthyl (**9**) to 2,2′-binaphthyl (**10**) upon exposure to $AlCl_3$ or $MoCl_5$.[9] Kuivila and co-workers later reported the same rearrangement when **9** was reacted at ambient temperature with TfOH in dichloromethane.[10] Binaphthyl derivatives have also been observed upon heating naphthalene with pure TfOH.[11] The high-temperature isomerization of binaphthyl isomers has also been reported.[12] The

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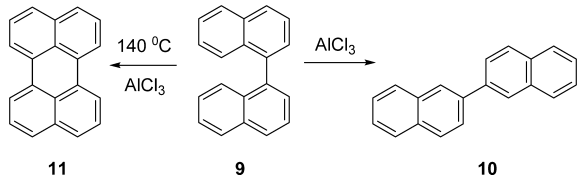
Scheme 2. Reported Reactions of Binaphthyl



solution-phase acid-catalyzed isomerization of phenylnaphthalene has not been reported; however, heating 1-phenylnaphthalene to 450 °C with acidic zeolites in the gas phase resulted in formation of 2-phenylnaphthalene as the major product, accompanied by small amounts of fluoranthene and naphthalene.[13] Structurally related cyclizations to fluoranthene are also known to occur upon heating with a H atom donor[12c] or with a chromia-alumina catalyst.[14]

In 1910, Scholl reported the formation of perylene (**11**) when either **9** or naphthalene was heated to 140 °C with $AlCl_3$ (Scheme 2).[15] This classic and often cited oxidative cyclization[16] involves the formation of an aryl−aryl bond and the elimination of two aryl-bound hydrogen atoms.[17] Scholl reaction conditions originally used Friedel−Crafts catalysts, with atmospheric oxygen likely to act as an oxidant.[15] Other conditions were later adopted to include an acid with an added oxidant; those include $AlCl_3/CuCl_2$,[18] $FeCl_3$,[19] $MoCl_5$,[20] $SbCl_5$,[21] $Tl(O_2CCF_3)_3$ in CF_3CO_2H or $BF_3{-}OEt_2$,[22] and CH_3SO_3H/DDQ.[23] As noted most clearly by King, acid-catalyzed rearrangements are well-known to occur under Scholl reaction conditions and can be problematic in designing the synthesis of polyarenes.[24] Arenium ion[25] and radical cation[23,26] mechanisms have been proposed for oxidative cyclizations similar to the Scholl reaction; it is likely that both mechanisms exist.[16,27]

The independent observations (Scheme 2) that 1,1′-binaphthyl isomerizes to **10**[9,10] but also cyclizes to perylene[15] would appear to be in conflict, implying a dynamic process. Our goal in the present study was to resolve this conflict and elucidate reaction mechanisms for both processes.

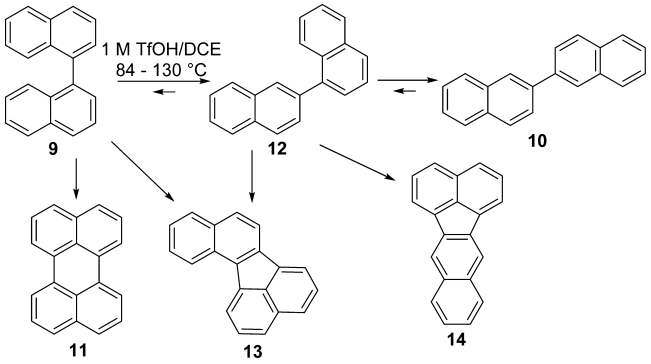
RESULTS AND DISCUSSION

We recently described the technique of microwave flash pyrolysis (MFP), in which high-temperature pyrolytic conditions are approached by heating mixtures of organic substances with graphite or carbon nanotubes in a microwave reactor.[28] MFP reaction of 1,1′-binaphthyl gave very little perylene, with naphthalene the major product. When we investigated either the solution- or solid-phase microwave reaction of 1,1′-binaphthyl with $AlCl_3$, 2,2′-binaphthyl proved to be the major product instead of perylene. This unexpected result prompted a more thorough investigation of rearrangement by acid catalysis.

Acid-Catalyzed Rearrangement and Cyclization of Binaphthyl Isomers. The original 1910 procedure described by Scholl involved heating **9** for 1 h at 140 °C with $AlCl_3$ under an atmosphere of dry air followed by cautious addition of water, boiling the crude product with concentrated aqueous HCl to complete hydrolysis, and then atmospheric pressure sublimation of the product at 350 °C! This procedure reportedly gave a 15% yield of yellow crystals which were assigned as perylene and represented its first synthesis.[15]

In repeating the initial steps in the Scholl reaction conditions,[15] we find that the heating stage of this reaction rapidly converts **9** to **10**, followed by slower formation of **11** and other minor products. As in our recent study with phenyl-substituted benzenes, 1 M TfOH in DCE proved to be optimal for observing these rearrangements.[4] Reactions were monitored by capillary GC and NMR with similar observed results. Under these conditions, 1,1′-binaphthyl (**9**) rearranged rapidly at ambient temperature to an equilibrium mixture (Scheme 3)

Scheme 3. Binaphthyl Rearrangement and Cyclization

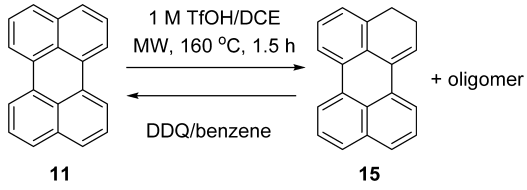


containing **9**, 1,2′-binaphthyl (**12**), and 2,2′-binaphthyl (**10**) in a ratio of <1:3:97. Essentially, the same equilibrium mixture resulted when this reaction was carried out beginning with any of the three isomers. Reduced acidity led to slower isomerization. These results support a sequential **9** to **12** to **10** transformation. At ambient temperature under nitrogen, no **11** was detected. When the reaction was run under 1 atm of oxygen, we observed 3% of **11** after 72 h at ambient temperature.

At reflux under nitrogen (84 °C), isomerization of **9** to **10** was too rapid to measure. Longer reaction times at reflux as well as heating in a microwave reactor to higher temperatures (100−160 °C) yielded primarily perylene (**11**) as product, accompanied by smaller amounts (9%) of benzo[*k*]-fluoranthene (**14**), the apparent product of cyclization of **12**. Benzo[*j*]fluoranthene (**13**) might also be formed by cyclization of **9** or **12**; only trace amounts (<1%) of **13** were observed by NMR analysis of product mixtures.

Along with isomerization and cyclization, minor dihydroaromatic products were formed at elevated temperature. 3,4-Dihydro-2,2′-binaphthyl was observed in small amounts from reaction at 130 °C in a microwave reactor, as identified by comparison to previously reported ^{1}H NMR data.[11] A more significant secondary product under MW or prolonged reflux conditions was assigned as 2,3-dihydroperylene (**15**). This has been reported previously as a product of electrochemical reduction of **11**.[29] The same product could be produced in ca. 50% yield upon heating pure **11** in 1 M TfOH/DCE at 160 °C (Scheme 4). Attempts at separating **15** from perylene were unsuccessful, and this substance easily aromatized. DDQ

Scheme 4. Formation of 2,3-Dihydroperylene



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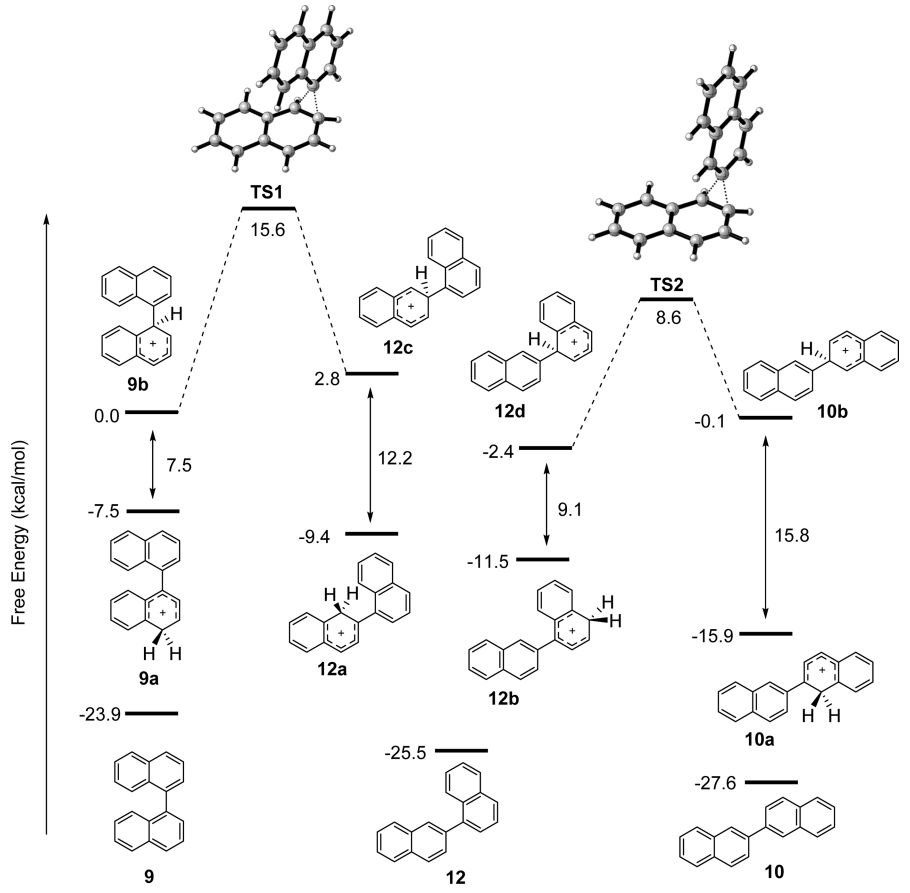
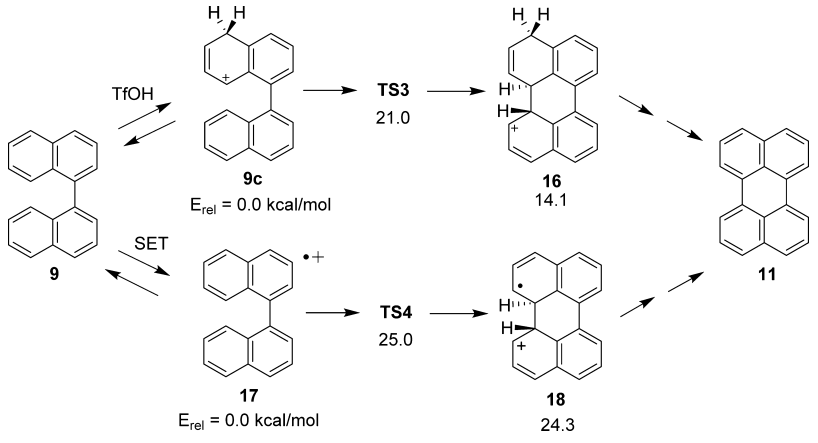


Figure 1. Energetics of protonation with TfOH and rearrangements of binaphthyl isomers in DCE.

Scheme 5. Energetics of Arenium Ion and Radical Cation Mechanisms for Cyclization to Perylene



oxidation of the **11** + **15** mixture yielded only **11**. We have recently shown that heating **11** with TfOH and DDQ in dichloromethane affords a high yield of quaterrylene, a product of further Scholl coupling.[30]

Computational Models for Binaphthyl Rearrangements. The energetics of protonation and the potential surface for rearrangements were investigated with density functional theory using Spartan 10[31] and Gaussian 09.[32] All calculations reported here are at the B3LYP/6-31+G(d,p) level of theory. This density functional has been widely used to study carbocation chemistry.[33] The polarizable continuum model (PCM) was employed to assess solvation in dichloroethane.[34]

The relative free energies of stationary points on this energy surface, with DCE solvation, are summarized in Figure 1. Energetics for the rearrangement of binaphthyl isomers follow a trend similar to those we have previously reported.[4] Solvation in DCE using PCM greatly stabilizes the carbocations for binaphthyl isomers compared to the energetics in vacuo, supporting a cationic mechanism in this medium. Because we are focusing on rearrangements, the combined solvated energies of cation **9b** + triflate anion have been chosen as an energy reference point, thus both the protonation steps and rearrangements share an energy scale. Predicted energetics for rearrangements are probably more reliable than absolute energies for protonation. The top portion of this figure

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represents interconversions among the *ipso* cations **9b**, **12c**, **12d**, and **10b**, which have modest barriers for naphthyl migration. 1,2-H shifts in arenium ions have low barriers[4] and should provide facile pathways to the lower-energy non-*ipso* cations **9a**, **12a**, **12b**, and **10a**.

In these reactions, all of the rearrangement steps must occur through higher-energy *ipso*-arenium ions.[4] A stepped sequence of naphthyl migrations with decreasing barriers follows initial formation of the *ipso*-arenium ion **9b**. Although cations **12c** and **12d** might interconvert by an inter-ring 1,2-shift, computations show a high barrier to this process, and thus neutral binaphthyl **12** must be an intermediate. The energetics in Figure 1 are consistent with the observed rapid isomerization of **9** and even faster isomerization of isomer **12** to **10**, with the latter structure favored at equilibrium. The lowest-energy carbocation **10a** is ultimately formed through an exothermic 1,2-H shift from **10b**. Energetics of the neutral isomers would favor **10** at equilibrium, as observed, but we believe it is more likely that relative cation stability is product-determining. Overall, Figure 1 must be considered to be a simple model for a very complex dynamic process; nevertheless, this seems to capture the essential features of our observed chemistry.

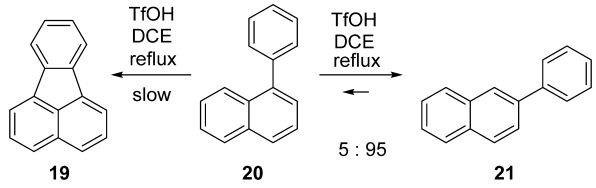
Although rearrangements almost certainly pass through *ipso*-arenium ions, the final cyclization to perylene can, in principle, occur through either intramolecular cyclization of an arenium ion or a radical cation. This is an ongoing debate in the mechanism for Scholl reactions.[16] Scheme 5 shows a direct comparison of the cyclization steps to intermediates of *trans* stereochemistry. This step is likely to be rate-determining in either mechanism. Computations for both pathways were carried out at the UB3LYP/6-31+G(d,p) level of theory with DCE solvation.

On the arenium ion pathway, protonation of **9c** followed by cyclization to **16** and deprotonation would proceed to a dihydroperylene. Aromatization can then occur through loss of hydride and subsequent deprotonation to yield **11**. There is ample precedent for proton and hydride transfers under strongly acidic conditions.[35] The radical ion mechanism is expected to proceed by cyclization of **17** to **18**, followed by deprotonation, a second one-electron oxidation of the radical, and then deprotonation. The barriers to these two cyclizations are very similar, but the cyclized radical cation **18** lies in a very shallow energy minimum. Electron transfer might also be coupled with deprotonation, and this could diminish the effective barrier for the radical ion mechanism. Given the many unknowns about other reaction steps, our calculations cannot distinguish between arenium ion and radical cation mechanisms for the final cyclization to perylene.

The same argument can be made about minor cyclization products **13** and **14**. Scholl products containing five-membered rings can be formed through cyclization of 1,1′-binaphthyl or 1,2′-binaphthyl to yield benzo[*j*]fluoranthene (**13**) or benzo[*k*]fluoranthene (**14**). The barriers for these cyclizations were calculated to be slightly higher than those for the cyclization to **11** (21−26 kcal/mol, Supporting Information Schemes S1−S3); however, the relative activation energies did not correlate with the minor amount of **14** formed and the trace of **13**. Overall product stability of the six-membered ring product versus that of the five-membered ring product is likely dictating the observed product formation. Starting with **10** or **12** did not change the ratio of cyclized products formed under microwave reaction conditions. Radical cation cyclizations to give **13** and **14** are predicted (Schemes S1−S3) to have barriers that are 7−9 kcal/mol higher than those for arenium ions.

Rearrangement and Cyclization of Phenylnaphthalene. Experimental results for the rearrangement and cyclization of phenylnaphthalene are outlined in Scheme 6.

Scheme 6. Rearrangement and Cyclization of Phenylnaphthalene



As expected, triflic acid catalysis at ambient temperature under nitrogen results in rapid phenyl migration, yielding a 5:95 mixture of **20** and **21**. At reflux, this mixture slowly transforms into fluoranthene (**19**).[13]

The energetics for initial rearrangement of phenylnaphthalene are summarized in Figure 2. The chosen reference point is

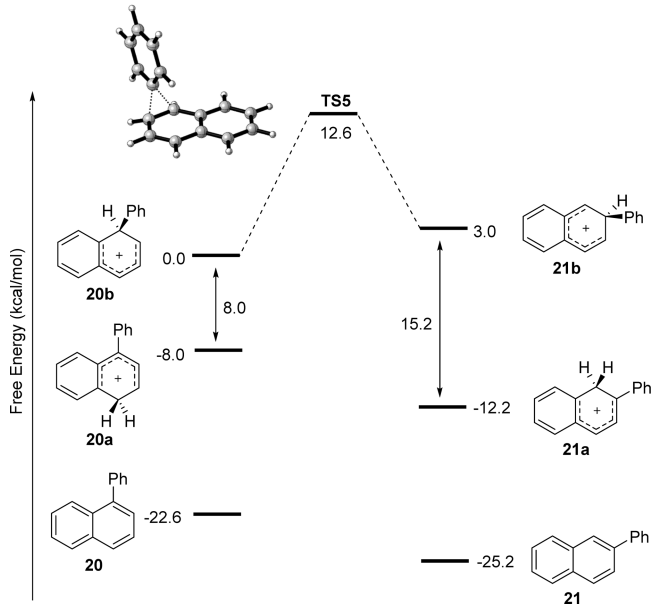


Figure 2. Energetics of protonation with TfOH and rearrangement of phenylnaphthalenes in DCE.

the *ipso* cation of 1-phenylnaphthalene (**20b**) + triflate anion in order to directly compare both rearrangement and protonation steps. The net barrier for this rearrangement from **20** to **21** is 20.6 kcal/mol (8.0 + 12.6), while the major product is formed through an exothermic 1,2-H shift from **21b** to **21a**.

Energetics for the cyclization to **19** have not been calculated; however, a mechanism similar to that of the cyclization of binaphthyl seems likely. Protonation of 1-phenylnaphthalene, followed by cyclization, would afford a protonated, dihydro derivative of fluoranthene. Deprotonation and loss of hydrogen would yield fluoranthene (**19**).

CONCLUSIONS

The cyclization of 1,1′-binaphthyl (**9**) to perylene (**11**)[15] is often cited as a classic Scholl reaction. As might have been deduced from earlier reports on the chemistry of **9**,[9,10] this

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reaction proceeds (Scheme 3) through interconversion with 1,2′- and 2,2′-binaphthyl isomers (**12** and **10**), with cyclization necessarily occurring from the low equilibrium concentration of **9**. Our experiments and DFT computational models support arenium ion mechanisms for rearrangements and are consistent with the rapid isomerization of **9** to **10**, with the intermediacy of **12**. We cannot distinguish between arenium ion and radical cation mechanisms for the final cyclization step to perylene. The presence of molecular oxygen effects a modest rate acceleration for cyclization, presumably by assisting the oxidation of a dihydroaromatic intermediate. Phenylnaphthalene also rearranges easily, with slower cyclization to fluoranthene. This has previously been observed over zeolites in the gas phase.[13] It is increasingly clear that arene rearrangements and oxidative cyclizations are inextricably linked.[16,24] In the present case, rearrangement provides an efficient synthesis of 2,2′-binaphthyl (**10**).

EXPERIMENTAL SECTION

General Methods. Trifluoromethanesulfonic acid (99% purity) and dichloroethane (99+%) were used as received from commercial sources. Glassware was oven-dried, and all reactions were run under a nitrogen atmosphere. ^{1}H NMR spectra were measured in $CDCl_3$ at 400 MHz and reported relative to TMS unless otherwise noted. Capillary analytical gas chromatography was performed using a DB-3 column (30 m × 0.320 mm), with temperature programming from 75 to 250 °C. Retention times were as follows: **9**, 18.4 min; **10**, 27.9 min; **11**, 43.0 min; **12**, 22.1 min; **14**, 35.6 min; **15**, 38.5 min; **19**, 17.2 min; **20**, 14.7 min; **21**, 15.8 min. Percentages are uncorrected for response factors. Microwave reactions were conducted in 10 mL vessels using a CEM Discover single-mode microwave reactor. 1,1′-Binaphthyl, perylene, and 1-phenylnaphthalene were commercial samples. The syntheses and NMR spectral data for 1,2′-binaphthyl,[36] 2,2′-binaphthyl,[37] and 2-phenylnaphthalene[38] have been reported previously.

General Procedure for Rearrangement under Reflux. A 25 mL, two-neck, round-bottom flask was equipped with a stir bar, water-cooled condenser, and glass stopper. Under a nitrogen atmosphere, the substrate (ca. 0.05 g) and DCE (4 mL) were charged to the flask. Trifluoromethanesulfonic acid (0.40 mL, 4.5 mmol) was added dropwise by syringe; this typically caused formation of a bright color due to formation of arenium ions.[4] The mixture was brought to reflux and monitored periodically by removal and analysis (^{1}H NMR or capillary GC) of small aliquots. Products were isolated by careful neutralization with saturated aqueous $NaHCO_3$ and extraction with dichloromethane unless otherwise noted.

General Procedure for Rearrangement in a Microwave Reactor. Under a nitrogen atmosphere, the substrate (ca. 0.05 g) and DCE (4 mL) were added to a 10 mL tube. Trifluoromethanesulfonic acid (0.40 mL, 4.5 mmol) was added dropwise by syringe; this typically caused formation of a bright color. The reaction mixture was capped and heated by microwave. Products were isolated by careful neutralization with saturated aqueous $NaHCO_3$ and extraction with dichloromethane, followed by analysis using ^{1}H NMR or capillary GC, unless otherwise noted.

Rearrangement and Cyclization of 1,1′-Binaphthyl (9). *Ambient Temperature.* 1,1′-Binaphthyl (**9**) rearranged rapidly (10 min) to 1,2′-binaphthyl (**12**) (3%) and 2,2′-binaphthyl (**10**) (97%) by capillary GC and ^{1}H NMR analysis. This equilibrium remained unchanged after 5 days at room temperature.

Reflux in DCE (84 °C). **9** rapidly reached initial equilibrium of binaphthyl isomers, followed by cyclization. After 24 h, the reaction mixture consisted of perylene (**11**) (73%), **10** (27%), and <1% **9**, 1,2′-binaphthyl (**12**), 3,4-dihydro-2,2′-binaphthyl, benzo[*k*]fluoranthene (**14**), and 2,3-dihydroperylene (**15**) by capillary GC and ^{1}H NMR analysis (82% mass recovery).

Microwave. Heating the reaction mixture in a microwave reactor (130 °C, 30 min) resulted in **11** (72%), **10** (11%), **14** (9%), **15** (8%), and <1% 1,1′-binaphthyl, 1,2′-binaphthyl, benzo[*j*]fluoranthene, and 3,4-dihydro-2,2′-binaphthyl by capillary GC and ^{1}H NMR analysis (89% mass recovery).

Rearrangement and Cyclization of 1,1′-Binaphthyl under O_2 Atmosphere. When the rearrangement of 1,1′-binaphthyl at ambient temperature was repeated under an O_2 atmosphere (1 atm), the formation of perylene (**11**) was observed after 24 h. After 4 days, **11** (3%), **10** (89%), **12** (7%), and **9** (1%) were observed by capillary GC and ^{1}H NMR analysis.

Observation of 1,2′-Binaphthyl (12) Intermediate with Reduced Acidity. **9** (0.02 g, 0.1 mmol), DCE (2 mL), and TfOH (18 μL, 2.0 mmol) were purged with N_2 and stirred at ambient temperature. After 1 h, the solution was neutralized with saturated $NaHCO_3$ and extracted using dichloromethane. Capillary GC analysis showed **9** (87%), **12** (2%), and **10** (11%).

Rearrangement and Cyclization of 2,2′-Binaphthyl (10). A mixture of **10** (0.05 g, 0.2 mmol), TfOH (0.40 mL, 4.5 mmol), and DCE (4 mL) was heated in a microwave reactor under N_2 (100 °C, 15 min). The resulting product distribution (90% mass recovery) was obtained by capillary GC and ^{1}H NMR analysis: **10** (83%), **11** (9%), **12** (8%), and **9** (<1%).

Formation of 2,3-Dihydroperylene (15). Perylene (**11**) (0.10 g, 0.40 mmol), DCE (4 mL), and TfOH (0.4 mL, 4.5 mmol) were mixed in a 10 mL reaction tube and purged with N_2. The reaction vessel was capped and placed in a microwave reactor (160 °C, 90 min). After the reaction time, the green/blue solution was neutralized with saturated $NaHCO_3$ and extracted using dichloromethane. Product was isolated as an orange solid (69% mass recovery) and was found to contain **11** (23%) and **15** (77%) by ^{1}H NMR analysis. 2,2-Dihydroperylene: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, 1H), 7.98 (d, 1H), 7.91 (d, 1H), 7.71 (dd, 2H), 7.48 (t, 2H), 7.30 (t, 1H), 7.16 (d, 1H), 6.73 (t, 1H), 2.90 (t, 2H), 2.56 (td, 2H). Calculated versus experimental ^{1}H NMR shifts can be seen in the Supporting Information (Figure S1).

Rearrangement and Cyclization of 1-Phenylnaphthalene (20). *Microwave.* **20** (0.10 g, 0.49 mmol), DCE (4 mL), and TfOH (9 μL, 1.0 mmol) were mixed in a 10 mL reaction tube and purged with N_2. The reaction vessel was capped and placed in a microwave reactor (115 °C, 30 min). After the reaction time, the solution was neutralized with saturated $NaHCO_3$ and extracted using dichloromethane. Capillary GC analysis showed **20** (5%) and 2-phenylnaphthalene (**21**) (95%).

Reflux. **20** rapidly rearranged to **21** via general refluxing conditions. After 4 h, the reaction mixture consisted of fluoranthene (**19**) (41%), **21** (57%), and **20** (2%) by capillary GC analysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01559.

Summary table of total energies and Cartesian coordinates for stationary points and selected spectra (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Baddeley, G. *J. Chem. Soc.* **1950**, 994−997. (b) Norris, J. F.; Vaala, G. T. *J. Am. Chem. Soc.* **1939**, *61* (8), 2131−2134. (c) Nightingale, D. V. *Chem. Rev.* **1939**, *25* (3), 329−376. (d) Olah, G. A.; Meyer, M. W.; Overchuk, N. A. *J. Org. Chem.* **1964**, *29* (8), 2310−12. (e) Olah, G. A.; Meyer, M. W.; Overchuk, N. A. *J. Org. Chem.* **1964**, *29* (8), 2313−2315.

(2) (a) Cram, D. J. *J. Am. Chem. Soc.* **1949**, *71*, 3863−70. (b) Bachmann, W. E.; Ferguson, J. W. *J. Am. Chem. Soc.* **1934**, *56*, 2081−4. (c) Allen, C. F. H.; Pingert, F. P. *J. Am. Chem. Soc.* **1942**, *64* (6), 1365−1371. (d) Wynberg, H.; Wolf, A. P. *J. Am. Chem. Soc.* **1963**, *85* (20), 3308. (e) Olah, G. A.; Meyer, M. W. *J. Org. Chem.* **1962**, *27*, 3682−3. (f) Olah, G. A.; Meyer, M. W. *J. Org. Chem.* **1963**, *28* (7), 1912−14. (g) Olah, G. A.; Lapierre, J. C. *J. Org. Chem.* **1966**, *31* (4), 1271−2. (h) Necula, A.; Racoveanu-Schiketanz, A.; Gheorghiu, M. D.; Scott, L. T. *J. Org. Chem.* **1995**, *60*, 3448−51.

(3) Kramer, G. M.; Skomoroski, R. M.; Hinlicky, J. A. *J. Org. Chem.* **1963**, *28* (8), 2085−6.

(4) Ajaz, A.; McLaughlin, E. C.; Skraba, S. L.; Thamatam, R.; Johnson, R. P. *J. Org. Chem.* **2012**, *77*, 9487−9495.

(5) Olah, G. A.; Surya Prakash, G. K.; Molnar, A.; Sommer, J. *Superacid Chemistry*, 2nd ed.; Wiley: New York, 2009.

(6) Perrin, C. L.; Skinner, G. A. *J. Am. Chem. Soc.* **1971**, *93* (14), 3389−3394.

(7) Olah, G. A.; Olah, J. A. *J. Am. Chem. Soc.* **1976**, *98* (7), 1839−42.

(8) Pritchard, R. G.; Steele, M.; Watkinson, M.; Whiting, A. *Tetrahedron Lett.* **2000**, *41* (35), 6915−6918.

(9) Kovacic, P.; Koch, F. W. *J. Org. Chem.* **1965**, *30* (9), 3176.

(10) Krishnamurti, R.; Kuivila, H. G.; Shaik, N. S.; Zubieta, J. *Organometallics* **1991**, *10* (2), 423−31.

(11) Launikonis, A.; Sasse, W.; Willing, I. *Aust. J. Chem.* **1993**, *46* (4), 427−440.

(12) (a) Copeland, P. G.; Dean, R. E.; McNeil, D. *J. Chem. Soc.* **1960**, 1689−1691. (b) Mayer, F.; Schiffner, R. *Ber. Dtsch. Chem. Ges. B* **1934**, *67B*, 67−69. (c) Senthilnathan, V. P.; Stein, S. E. *J. Org. Chem.* **1988**, *53* (13), 3000−3007.

(13) Perez, G.; Raimondo, M. *Chemosphere* **1996**, *32*, 1301−5.

(14) Orchin, M.; Reggel, L. *J. Am. Chem. Soc.* **1947**, *69*, 505−9.

(15) Scholl, R.; Seer, C.; Weitzenbock, R. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 2202−9.

(16) Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T. *Angew. Chem., Int. Ed.* **2013**, *52* (38), 9900−9930.

(17) Balaban, A. T.; Nenitzescu, C. D. Scholl and Related Reactions. In *Friedel−Crafts and Related Reactions. Alkylation and Related Reactions, Part 2*; Olah, G. A., Ed.; Interscience Publishers: New York, 1964; Vol. *II*, Chapter XXIII.

(18) Kovacic, P.; Kyriakis, A. *J. Am. Chem. Soc.* **1963**, *85*, 454−8.

(19) Kovacic, P.; Kyriakis, A. *Tetrahedron Lett.* **1962**, *3* (11), 467−469.

(20) Kramer, B.; Fröhlich, R.; Waldvogel, S. R. *Eur. J. Org. Chem.* **2003**, *2003* (18), 3549−3554.

(21) Yamaguchi, S.; Swager, T. M. *J. Am. Chem. Soc.* **2001**, *123*, 12087−12088.

(22) McKillop, A.; Turrell, A. G.; Young, D. W.; Taylor, E. C. *J. Am. Chem. Soc.* **1980**, *102*, 6504−12.

(23) Zhai, L.; Shukla, R.; Rathore, R. *Org. Lett.* **2009**, *11* (15), 3474−3477.

(24) Ormsby, J. L.; Black, T. D.; Hilton, C. L.; Bharat; King, B. T. *Tetrahedron* **2008**, *64*, 11370−11378.

(25) Nenitzescu, C. D.; Balaban, A. *Chem. Ber.* **1958**, *91*, 2109−16.

(26) Rooney, J. J.; Pink, R. C. *Proc. Chem. Soc., London* **1961**, 142−143.

(27) (a) Rempala, P.; Kroulik, J.; King, B. T. *J. Am. Chem. Soc.* **2004**, *126* (46), 15002−15003. (b) Rempala, P.; Kroulik, J.; King, B. T. *J. Org. Chem.* **2006**, *71* (14), 5067−5081.

(28) Cho, H. Y.; Ajaz, A.; Himali, D.; Waske, P. A.; Johnson, R. P. *J. Org. Chem.* **2009**, *74* (11), 4137−4142.

(29) (a) Coffield, J. E.; Mamantov, G.; Zingg, S. P.; Smith, G. P.; Buchanan, A. C., III *J. Electrochem. Soc.* **1992**, *139*, 355−359. (b) Rampazzo, L.; Zeppa, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *105*, 221−4.

(30) Thamatam, R.; Skraba, S. L.; Johnson, R. P. *Chem. Commun.* **2013**, *49* (80), 9122−9124.

(31) *Spartan 10*; Wavefunction Inc.: Irvine, CA.

(32) Frisch, M. J.; et al. *Gaussian 09*, revision B.01; Gaussian Inc.: Wallingford, CT, 2010.

(33) (a) Aue, D. H. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2011**, *1* (4), 487−508. (b) Lodewyk, M. W.; Gutta, P.; Tantillo, D. J. *J. Org. Chem.* **2008**, *73* (17), 6570−6579. (c) Hong, Y. J.; Tantillo, D. J. *J. Am. Chem. Soc.* **2014**, *136*, 2450.

(34) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105* (8), 2999−3094.

(35) (a) Deshmukh, R. R.; Lee, J. W.; Shin, U. S.; Lee, J. Y.; Song, C. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 8615−8617. (b) Kantner, S. S.; Kreevoy, M. M. *J. Org. Chem.* **1977**, *42*, 865−8. (c) Kuck, D. *Eur. Mass Spectrom.* **2012**, *18*, 161−181. (d) Mayr, H.; Lang, G.; Ofial, A. R. *J. Am. Chem. Soc.* **2002**, *124*, 4076−4083.

(36) Chen, H.; Huang, Z.; Hu, X.; Tang, G.; Xu, P.; Zhao, Y.; Cheng, C.-H. *J. Org. Chem.* **2011**, *76*, 2338−2344.

(37) Nising, C. F.; Schmid, U. K.; Nieger, M.; Bräse, S. *J. Org. Chem.* **2004**, *69* (20), 6830−6833.

(38) Shen, H.-C.; Pal, S.; Lian, J.-J.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 15762−15763.

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