Preparation of Condensed Aromatics by Superacidic Dehydrative Cyclization of Aryl Pinacols and Epoxides[1a]

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Received February 14, 1997 (Revised Manuscript Received July 18, 1997[⊗])

Aryl pinacols and epoxides, respectively, are cleanly and in high yield converted via superacidic dehydrative cyclization to the corresponding condensed aromatics. Dehydrative cyclization of benzopinacol (**1a**), triphenylacetophenone (**2**), and tetraphenylethylene oxide (**9**) give 9,10-diphenylphenanthrene (**3a**) as the major product in acidic media stronger than $H_o = -11$. Aryl pinacol **12a** forms the condensed aromatic **13a** as the major product in acidic media stronger than $H_o = -13.5$. It is proposed that the dehydrative cyclizations to provide aromatics **3a** and **13a** occurs through dicationic intermediates. Substituted benzopinacols **1f**, **1g**, and **1j** are prepared and give the corresponding phenanthrenes (**3f**, **3g**, and **3j**) in high yields. The regiochemistry of the cyclization of substituted benzopinacols is controlled by deactivating substituents on the aryl rings. Aryl pinacols (**12a**−**d**) derived from acenaphthenequinone and pinacol **15** also give condensed aromatics (**13a**−**d** and **16**, repectively) with superacidic triflic acid.

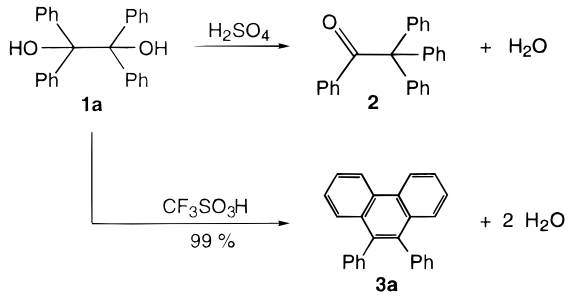
Introduction

When pinacols are reacted with acids, dehydration and rearrangement products arise.[2] This well-known reaction is generally refered to as the pinacol rearrangement. The pinacol rearrangement can be promoted by both Bronsted and Lewis acids, and the reaction is general to many types pinacols or 1,2-diols.[3a] When benzopinacol (**1a**) is reacted with acids of moderate strength, the pinacol rearrangement leads to 2,2,2-triphenylacetophenone (**2**) in high yield.[3b] It is also well-known that appropriate epoxides with acids undergo similar ring-opening rearrangement to products such as **2**.[3c,d,f] Recently, we found that benzopinacol (**1a**) and substituted benzopinacols (**1b**,**c**,**d**,**h**,**i**) react in triflic acid (TfOH) to yield 9,10-diphenylphenanthrene (**3a**) and substituted 9,10-diarylphenanthrenes in excellent yield.[4,5] We now report studies on the general dehydrative condensation of aryl pinacols and related epoxides to condensed aromatics in superacids and their mechanism which involves superelectrophilic, dicationic intermediates.

Results and Discussion

Depending on the strength of the acid catalyst, benzopinacol (**1a**) gives either **2** or **3a** by elimination of one or two molecules of water, respectively. With superacidic TfOH ($H_o = -14.1$),[6b] **2** itself gives **3a**. Since weaker acid systems convert **1a** to **2**, the question arises as to the level of acidity that is required for the conversion of **2** to **3a**. A series of reactions was carried out using the TfOH/CF_3CO_2H system[6a] of increasing acidity in order to establish the threshold level of acid strength needed for conversion of **2** to **3a**. These results are presented in Table 1. In the different acid systems, only **3a** was formed from **2** when the acid strength exceeded about $H_o = -11$.[6b] Benzopinacol (**1a**) was also reacted in the TfOH/CF_3CO_2H acid systems to verify that the results for **2** were similar to those of **1a**. As shown in Table 1, product **3a** is formed exclusively in acid systems with strengths greater than $H_o = -12$ (i.e., with superacids).

Shudo and co-workers recently reported that a phenyl ketone similar to **2** is fully protonated in acidic medium stronger than $H_o = -9$.[7a] In more strongly acidic media, there is the possibility for further protonation of the



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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

(1) (a) Chemistry in Superacids. 23. For part 22, see: Olah, G. A.; Rasul, G. *J. Am. Chem. Soc.* **1996**, *118*, 8503. (b) Undergraduate research participant.

(2) (a) Rickborn, B. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 3, p 721. (b) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 1072. (c) Collins, C. J. *Q. Rev.* **1960**, *14*, 357.

(3) (a) Bartok, M.; Molnar, A. In *The Chemistry of Functional Groups*; Patai, S., Ed.; Wiley: New York, 1980; Suppl. E; p 721. (b) Bachmann, W. E. *Organic Syntheses*; Blatt, A. H., Ed.; Wiley: New York, 1943; Collect. Vol. 2, p 73. (c) Pocker, Y.; Ronald, B. P. *J. Org. Chem.* **1970**, *35*, 3362. (d) Gebhart, H. J., Jr.; Adams, K. H. *J. Am. Chem Soc.* **1954**, *76* , 3925. (e) Hill, G. A.; Flosdorf, E. W. *Organic Syntheses*, Gilman, H., Ed.; Wiley: New York, 1941; Collect. Vol. 1, 2nd ed.; p 462. (f) Pocket, Y.; Ronald, B. P. *J. Am. Chem Soc.* **1970**, *92*, 3385.

(4) Olah, G. A.; Klumpp, D. A.; Neyer, G.; Wang, Q. *Synthesis* **1996**, 321. For a review of triflic acid chemistry, see: Stang, P. J.; White, M. R. *Aldrichimica Acta* **1983**, *16*, 15.

(5) Olah, G. A.; Klumpp, D. A. *Abstract of Papers*, 211st National Meeting of the American Chemical Society, Chicago, IL, August 1995; American Chemical Society: Washington, DC, 1995; Abstract ORGN 17.

(6) (a) Saito, S.; Saito, S.-i.; Ohwada, T.; Shudo, K. *Chem. Pharm. Bull.* **1991**, *39*, 2718. (b) For a general discussion of superacids, see: Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985.

(7) (a) Saito, S.; Sato, Y.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1994**, *116*, 2312. (b) Shudo, K.; Ohwada, T. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; Wiley: New York, 1997; pp 540−541.

(8) (a) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767. (b) Ohwada, T.; Yagamata, N.; Shudo, K. *J. Am. Chem. Soc.* **1991**, *113*, 1364. (c) Yamazaki, T.; Saito, S.-i.; Ohwada, T.; Shudo, K. *Tetrahedron Lett.* **1995**, *36*, 5749. (d) Olah, G. A.; Ramaiah, P.; Wang, Q.; Prakash, G. K. S. *J. Org. Chem.* **1993**, *58*, 6900. (e) Hartz, N.; Rasul, G.; Olah, G. A. *J. Am. Chem. Soc.* **1993**, *155*, 1277. (f) Olah, G. A.; Rasul, G.; Aniszfeld, R.; Prakash, G. K. S. *J. Am Chem. Soc.* **1992**, *114*, 5608. (g) Berkessel, A.; Thauer, R. K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2247.

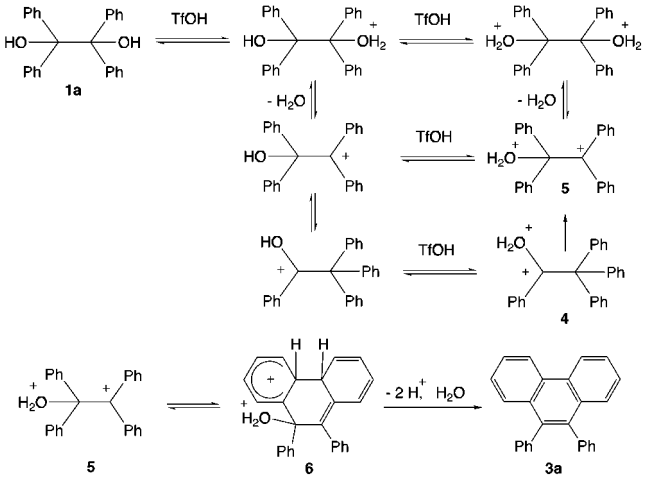
S0022-3263(97)00293-4 CCC: $14.00

Table 1. Results of the CF_3SO_3H:CF_3CO_2H-Catalyzed Reaction of 1a, 2, and 9[a]

starting material	H_o[6]	TfOH/CF_3CO_2H % w/w	products **2**:**3a**
2	−14.1	100% TfOH	0:100
2	−12.5	72.8	0:100
2	−11.5	43.5	30:70
2	−10.6	22.1	100:0
2	−2.7	100% CF_3CO_2H	100:0
1a	−14.1	100% TfOH	0:100
1a	−12.5	72.8	0:100
1a	−11.5	43.5	29:71
1a	−10.6	22.1	40:60
1a	−2.7	100% CF_3CO_2H	100:0
9	−14.1	100% TfOH	0:100
9	−12.5	72.8	8:91
9	−11.5	43.5	42:58
9	−10.6	22.1	95:5
9	−2.7	100% CF_3CO_2H	100:0

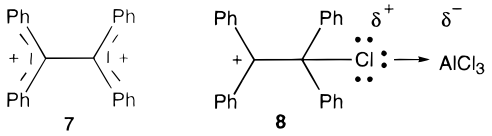
[a] Product ratio determined by ^1H NMR integration; Reaction conditions: 50 mg starting material, 0.5 mL C_6H_6 and 0.5 mL acid (24 h at 25 °C).

Scheme 1. Proposed Mechanism for the Formation of 3a from 1a

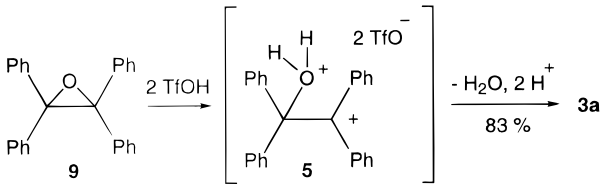


carbonyl group. Protosolvolytic activation of onium ions has been studied extensively by Olah, Shudo, and others.[8] Protosolvated intermediates may behave as highly reactive electrophiles, or superelectrophiles. Since **1a** and **2** give **3** only in strongly acidic media (H_o < −11) and phenyl ketones are known to be fully protonated in less acidic media, this indicates a protosolvated reactive intermediate to be involved in the transformation of **1a** to give **3a**.

The proposed mechanism for this conversion is shown in Scheme 1. We suggest that the dication **5** is the reactive intermediate which leads to cyclization giving **6** followed by dehydration to yield **3a**. It also could be that the dicationic intermediate **4** induces a retropinacol rearrangement to give **5**. There is reported evidence for epoxide intermediates in pinacol rearrangements,[3d,f] and these intermediates may also participate in the formation of **3a**. Alternatively, **5** may dehydrate to provide tetraphenylethylene dication (**7**), which is known to form **3a**.[9] It was reported that 1,2-dichlorotetraphenylethane gives **3a** when reacted with an excess of $AlCl_3$.[10] This conversion may proceed through dication **7**, or through a cation, donor−acceptor complex (**8**) which however itself possesses significant dicationic nature.



Like benzopinacol, tetraphenylethylene oxide (**9**) also gives **3a** in good yield when reacted with TfOH. The conversion of **9** to form **3a** can be rationalized by the protonation of the epoxide oxygen, followed by ring opening, and subsequent protonation of the oxygen to give the dicationic intermediate **5**. When **9** was reacted in the TfOH/CF_3CO_2H acid systems of varying strength (Table 1), product **3a** was formed exclusively only in superacidic media of H_o < −12.5. In less acidic media, the ketone **2** was formed in greater amounts. These observations are consistant with the formation of a dicationic intermediate, such as **5**, and are in accord with the results of reactions from **1a** and **2**.

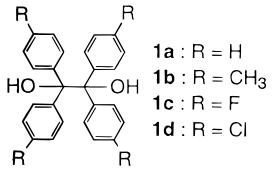


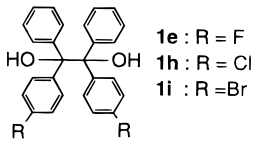
The results from **9**, **1a**, and **2** indicate that highly acidic media are necessary to form **3a** as the exclusive product. Since lower levels of acidity involve the intermediacy of monocations, the results indicate that the highly acidic media allow the formation of dicationic intermediates which results in the dehydrative cyclization giving **3a**. While superelectrophilic activation is recognized for intermolecular reactions, few examples have been reported of intramolecular conversions involving dicationic, superelectrophiles. Shudo and co-workers described the cyclodehydration of 1,3-diaryl-1-propanones in superacid to provide substituted indenes.[7a] In these studies, the yields of indene products and cyclization rates increased dramatically in acid systems stronger than H_o = −10, suggesting dicationic intermediates. In another study, Shudo found evidence for superelectrophilic activation in the intramolecular reaction of a nitrile with a phenyl group.[7b] The earlier work by Shudo and the present results indicate that superelectrophilic activation may be synthetically useful for intramolecular cyclizations leading to condensed products.

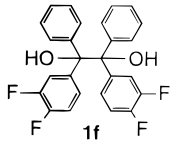
Wishing to explore the synthetic scope of the pinacol conversion in superacids, we prepared a series of aryl pinacols from substituted benzophenones and reacted them in TfOH. The results from these studies are presented in Table 2. In most cases, the aryl pinacols gave the condensed arenes in excellent yield. The substituted benzopinacols **1b** to **1d** yielded the corresponding phenanthrenes **3b** to **3d** sometimes in quantitative yield when reacted in TfOH. When the aryl pinacols are substituted on just two of the aryl rings,

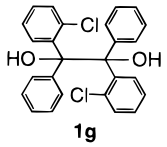
(9) (a) Olah, G. A.; Grant, J. L.; Spear, R. J.; Bollinger, J. M.; Serianz, A.; Sipor, G. *J. Am. Chem. Soc.* **1976**, *98* , 2501. (b) As suggested by a referee, the cyclization of **7** may be thought of as an electrocyclization reaction followed by the loss of two protons. This cyclization mechanism may also explain the observed regioselectivity in the formation of products **3f**−**j**. A dication such as **7** would tend to delocalize positive charge into the more electron rich rings, which would then cyclize and lead to products **3f**−**j**.

(10) (a) Schmidlin, J.; Escher, R. *Chem. Ber.* **1910**, *43*, 1153. (b) Schoepfle, C. S.; Ryan, J. D. *J. Am. Chem. Soc.* **1932**, *54*, 3687.

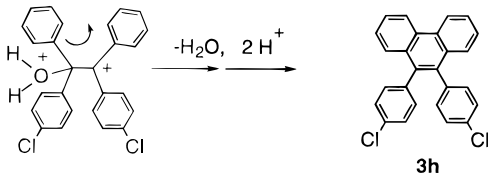




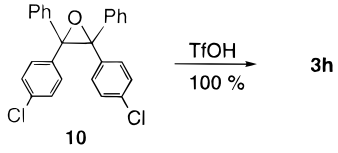




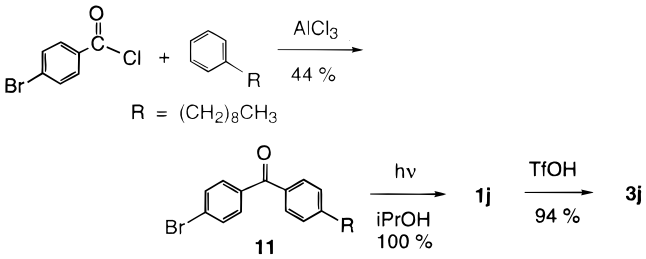
there is the possibility of several regioisomers being formed. Pinacol **1e** gives a mixture of isomeric phenanthrenes, and the overall yield of products is high. NMR evidence suggests the formation of at least three isomers. This indicates cyclization to form the phenanthrenes proceeding through both the phenyl and fluorophenyl rings. However, when the two aryl rings are substituted by a pair of fluorine atoms (**1f**) phenanthrene **3f** is formed regioselectively (Table 2). Similarly when the aryl rings are substituted by more strongly deactivating groups, such as chloro and bromo substituents in pinacols **1h** and **1i**, phenanthrenes **3h** and **3i** are formed regioselectively and in high yields. These data suggest that the cyclization to the phenanthrenes is occurring more rapidly through the unsubstituted phenyl rings than through the substituted deactivated ones. This is consistant with the fact that chloro and bromo substituents are stronger deactivating groups than a fluoro substituent and that deactivating groups retard the rate of electrophilic reactions with aryl rings.[11] In the case of **1e** and **1f**, one fluorine (**1e**) does not allow for regioselective product formation, but two fluorines (**1f**) deactivate the substituted rings sufficiently to provide good regioselectivity.



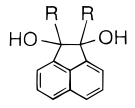
It was also found that epoxide **10** gave **3h** in quantitative yield. Consequently epoxides with deactivating substituent groups may also allow regioselective product formation of substituted phenanthrenes.



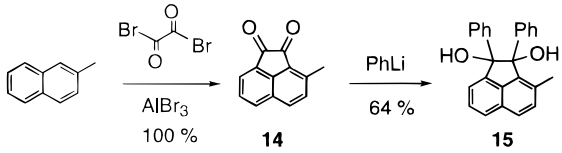
As a further demonstration of regiocontrol in the pinacol cyclization, pinacol **1j** was found to give the nonyl-substituted phenanthrene **3j** as a single regioisomer in high yield (Table 2). Pinacol **1j** was prepared by the acylation of 1-phenylnonane, followed by the photolysis of the aryl ketone. **1j** was produced as the meso-*dl* diastereomeric pair, and the mixture of stereoisomers gave the single product **3j** with TfOH. The bromophenyl groups are deactivated relative to the alkylphenyl groups in **1j**, and thus the regiocontrol is maintained in the reaction.

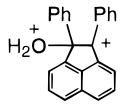


Some pinacols have also been prepared by the reaction of aryl Grignard and lithium reagents with acenaphthenequinone and these derivatives (**12a**−**d**) gave condensed aromatic products **13a**−**d** (Table 3). Pinacol **15** could be prepared in good yield from 2-methylnaphthalene,[25] and **15** provides aromatic **16** with TfOH. Like benzopinacol (**1a**), **12a** undergoes dehydrative cyclization leading to a condensed aromatic product. When **12a** was reacted in acid systems of varying strength, **13a** was only formed in superacidic media, $H_o < -12$ (Table 4). If an analogy is made with the related studies with **1a**, the data with **12a** suggest a dicationic intermediate such as **17** leading to a cyclization to eventually form product **13a**. Aryl pinacols **12a**−**d** and **15** provided the expected aromatic products **13a**−**d** and **16**, respectively; however, the yields of these product were somewhat lower than those from benzopinacols **1a**−**i**. Products **13a**−**d** and **16** were sometimes accompanied by the formation of varying amounts of insoluble polymer and other byproducts. Nevertheless, the results in Table 3 demonstrate that the dehydrative cyclization of aryl pinacols in superacid is a useful route to structurally diverse aromatic products.

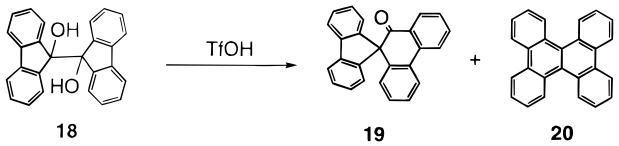


12a : R = Phenyl
12b : R = 4-Fluorophenyl
12c : R = 4-Methylphenyl
12d : R = 1-Naphthyl



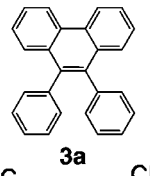
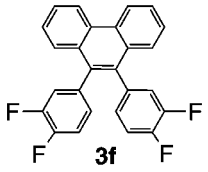
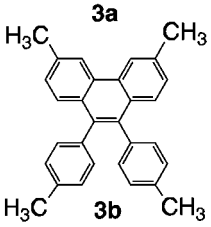
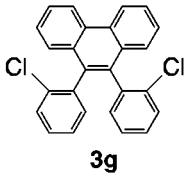
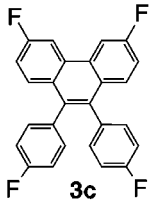
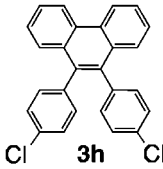
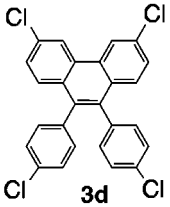
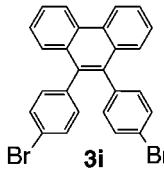
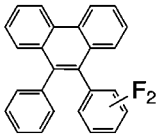
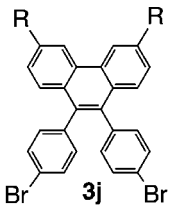


When pinacol **18** was reacted with TfOH, the expected dehydrative cyclization product was not formed and **19** and **20** were obtained. **19** is the product from the pinacol rearrangement, and it is produced in greater than 80% yield with reaction times of 2 h or less. However, with longer reaction times, **20** is the major product and is



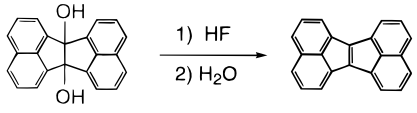
(11) (a) Gore, P. H. In *Freidel-Crafts and Related Reactions*; Olah. G. A., Ed.; Interscience: New York, 1964; Vol. 3, Chapter 31. (b) Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, 1990; Chapter 2.

Table 2. Triflic Acid Catalyzed Reaction of Aryl Pinacols 1a–j

Pinacol	Product	Yield	Pinacol	Product	Yield
1a	 **3a**	99 %[a]	**1f**	 **3f**	70 %
1b	 **3b**	90 %[a]	**1g**	 **3g**	100 %
1c	 **3c**	95 %[a]	**1h**	 **3h**	98 %[a]
1d	 **3d**	100 %[a]	**1i**	 **3i**	87 %[a]
1e		100 % (Mixture of Isomers)	**1j**	 **3j** R = $(CH_2)_8CH_3$	94 %

[a]Reference 4

obtained in greater than 90% yield. If **19** is isolated and reacted with TfOH, **20** is formed. The identity of **20** was unambigously verified by its X-ray crystal structure[12] as well as its ^1H, ^{13}C, and HETCOR NMR spectra. Although it is not exactly clear how **20** arises, the ring system is likely generated by ring expansion involving the protonated carbonyl group of **19**. The formation of **20** is similar to the formation of aromatic **22** from **21** in anhydrous HF.[13] In this work, it was suggested that **22** may be formed via a dicationic intermediate followed by electron transfer reactions to give the final product.



21 22

(12) Crystallographic data: colorless prism; crystal size (mm) 0.25 × 0.4 × 0.75; monoclinic; space group $P2_1/n$; unit cell dimensions (Å), a = 12.172 (2), b = 7.628, c = 17.691(2); β = 97.40 (2)°; volume 1628.9 (5) Å ^{3}; R = 0.07.

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

Conclusions

It was shown that aryl pinacols **1a–d** and **1f–j** yield in superacidic TfOH substituted phenanthrenes **3a–d** and **3f–j**, repectively, in excellent yield. Aryl epoxides **9** and **10** also give substituted phenanthrenes (**3a** and **3h**) under similar conditions. The regiochemistry of products obtained can be controlled by deactivating groups on the aryl rings. The results suggest that dicationic intermediates are involved, inducing a cyclization leading to products. Experiments showed that the reaction medium must be of acid strength greater than $H_o = -12$, i.e., superacidic, for effective conversion to the phenanthrene **3a** from **1a**, **2**, or **9**. Aryl pinacols **12a–d** and **15** also gave condensed aromatics **13a–d** and **16**, respectively, in fair to good yields. The acid system must be again more acidic than $H_o = -12$ for the conversion **12a** to **13a**, suggesting the necessity of dicationic intermediates leading to **13a**. The described reactions of aryl pinacols in superacidic TfOH are an effective synthetic method to condensed aromatics.

Table 3. Triflic Acid Catalyzed Reaction of Aryl Pinacols 12a–d and 15

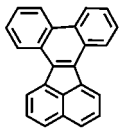
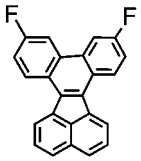
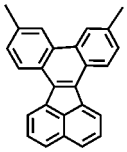
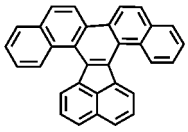
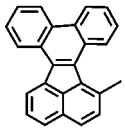
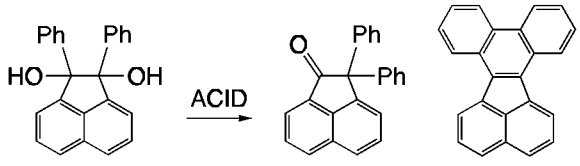
Pinacol	Product	% Yield
12a	 **13a**	72 %
12b	 **13b**	47 %
12c	 **13c**	21 %
12d	 **13d**	39 %
15	 **16**	21 %

Table 4. CF_3SO_3H:CF_3CO_2H-Catalyzed Reaction of 12a[a]



12a **14** **13a**

Starting Material	H_o[6]	TfOH/CF_3CO_2H % w/w	Products **14** : **13a**
12a	-14.1	100 % TfOH	0 : 100
12a	-13.5	98.2	2 : 98
12a	-12.5	72.8	97 : 3
12a	-11.5	43.5	100 : 0
12a	-10.6	22.1	100 : 0
12a	-2.7	100 % CF_3CO_2H	100 : 0

[a]Product ratio determined by ^{1}H NMR integration; Reaction conditions : 50 mg starting material, 0.5 mL C_6H_6 and 0.5 mL acid (24 hrs at 25°C).

Experimental Section

Melting points are uncorrected. Unless otherwise noted, ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz. High-resolution mass spectra were recorded at the Southern California Mass Spectrometry Facility, University of California, Riverside. Elemental analyses were performed at Galbraith Laboratories, Knoxville, TN. Solvents were dried according to standard procedures.[14] Column chromatography was done with Merck silica gel (grade 9385) according to standard procedures.[15] Triflic acid was obtained from 3M and distilled prior to use. Benzopinacol (**1a**), aryl ketones, acenaphthenequinone, phenylmagnesium bromide, *p*-tolylmagnesium bromide, and (4-fluorophenyl)magnesiumbromide were obtained from Aldrich and used as received; 3,4-difluorobenzophenone was purchased from Lancaster; and pinacols **1b–j** were prepared by photolysis of the appropriate aryl ketones. Photochemical preparations were accomplished with a 450 W medium pressure Hg vapor lamp (Pyrex filter).

General Photolysis Procedure[16] for the Preparation of Aryl Pinacols 1b–j. The aryl ketone was dissolved (0.1 M) in degassed 2-propanol and the solution placed a Pyrex tube under an argon or nitrogen atmosphere. Photolysis was done at room temperature, and product formation was monitored by thin layer chromatography. Upon completion of the photolysis (typically less than 6 h reaction time), the product was isolated either by filtration of precipitated product, or by concentration *in vacuo*.

1,2-Bis(3,4-difluorophenyl)-1,2-diphenyl-1,2-ethanediol (1f). Using the general photolysis procedure, 3,4-difluorobenzophenone (0.40 g, 1.8 mmol) gave **1f** (0.79 g, 100%) as a viscous oil (mixture of diastereomers).

1,2-Bis(4-bromophenyl)-1,2-bis(4-nonylphenyl)-1,2-ethanediol (1j). Using the general photolysis procedure, **11** (0.72 g, 1.9 mmol) gave **1j** (0.74 g, 100%), which was purifed by column chromatography (19:1 hexane:Et_2O) to give the mixture of diastereomers as a viscous oil.

9,10-Diphenylphenanthrene (3a). Epoxide **9** (0.325 g, 0.76 mmol) was prepared according to a published procedure[17] and was added to 5 mL of TfOH. The mixture was stirred for 8 h at 25 °C, poured over ca. 10 g of ice, and extracted twice with C_6H_6. The organic phase was washed with water and then brine and dried over $MgSO_4$. Concentration *in vacuo* and recrystallization from CH_2Cl_2 gave **3a**[18] (0.208 g, 83%).

9,10-Bis(4-chlorophenyl)phenanthrene (3h). Epoxide **10** (0.202 g, 0.49 mmol) was prepared according to a published procedure[19] and dissolved in 2 mL of C_6H_6. The solution of **10** was added to 5 mL of TfOH. The mixture was stirred for 8 h at 25 °C, poured over ca. 10 g of ice, and extracted twice with C_6H_6. The organic phase was washed with water and then brine and dried over $MgSO_4$. Concentration *in vacuo* gave **3h**[18] (0.20 g, 100%).

9,10-Bis(3,4-difluorophenyl)phenanthrene (3f).[20] To 5 mL of TfOH, **1f** (0.35 g, 0.8 mmol) was added. The mixture was stirred for 8 h at 25 °C, poured over ca. 10 g of ice, and extracted twice with C_6H_6. The organic phase was washed with water and then brine and dried over $MgSO_4$. Concentration *in vacuo* and purification by preparative thin layer chromatography (9:1 hexane:Et_2O) gave **3f** (0.23 g, 70%) as pale yellow crystals.

(14) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.
(15) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(16) (a) Schonburg, A.; Mustafa, A. *Chem. Rev.* **1947**, *40*, 181. (b) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; CRC Press: Boca Raton, FL, 1991; p 302.
(17) Zeigler, H. E.; Wo, S. *J. Org. Chem.* **1995**, *60*, 5925.
(18) Analytical data found in ref 4.
(19) Sato, R.; Nagaoka, T.; Saito, M. *Tetrahedron Lett.* **1990**, *31*, 5749.
(20) Products **3f** and **3g** exhibited complex NMR spectra at ambient temperature, suggesting that the aryl rings in the 9,10 positions of the phenanthrenes possess restricted rotation.

9,10-Bis(2-chlorophenyl)phenanthrene (3g).[20] Using a similar procedure to that of **3f**, **1g**[21] (0.15 g, 0.34 mmol) gave **3g** (0.14 g, 100%) as a white solid.

9,10-Bis(4-bromophenyl)-3,6-dinonylphenanthrene (3j). To a mixture of **1j** (0.27 g, 0.35 mmol) in 5 mL of C_6H_6 was added TfOH (10 mL), and the solution was stirred for 12 h at 25 °C. After workup similar to that of for **3f**, and column chromatography with hexanes, **3j** (0.24 g, 86%) was isolated as a waxy, white solid.

4-Bromo-4′-nonylbenzophenone (11). To a mixture of 1-phenylnonane (1.53 mL, 6.4 mmol) and anhydrous $AlCl_3$ (0.9 g, 6.8 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added a solution of 4-bromobenzoyl chloride (1.4 g, 6.4 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at 25 °C for 8 h, then poured over ca. 20 g of ice, extracted into CH_2Cl_2, and washed with dilute HCl, H_2O, and then brine. After drying over $MgSO_4$ and concentrating *in vacuo*, the crude product mixture was purified by column chromatography (19:1 hexane:Et_2O). **11** was isolated (1.1 g, 44%) as a white solid: mp 48−51 °C; ^{1}H NMR ($CDCl_3$) δ 0.82−0.92 (m, 3H), 1.16−1.38 (m, 14H), 2.70 (t, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.6, 29.2, 29.4, 29.5, 31.1, 31.5, 31.8, 36.0, 127.1, 128.3, 130.1, 131.3, 131.4, 134.5, 136.6, 148.4, 195.1; HRMS calcd for $C_{22}H_{27}OBr$ 386.1245, found 386.1239

1,2-Dihydroxy-1,2-bis(4-fluorophenyl)acenaphthene (12b). To a solution of (4-fluorophenyl)magnesium bromide (11 mmol) in 25 mL of THF at 0 °C was added acenaphthenequinone (0.50 g, 2.7 mmol). The mixture was stirred at 25 °C for 12 h and then poured into a dilute solution of H_2SO_4. The resulting mixture was extracted into ether, and the organic extracts were washed with $NaHCO_3$, brine, and dried with $MgSO_4$. After column chromatography with hexanes:ether (4:1), **12b** (0.43 g, 42%) was isolated as a white solid: mp 184−185 °C; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 2H), 7.03 (m, 4H), 7.21 (m, 4H), 7.34 (d, J = 6.9 Hz, 2H), 7.65 (m, 2H), 7.34 (d, J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 89.3, 114.7 (d, J_{C-F} = 21 Hz), 121.7, 125.6, 129.0, 129.7 (d, J_{C-F} = 8.0 Hz), 131.2, 136.1 (d, J_{C-F} = 4.0 Hz), 137.0, 145.2, 162.5 (d, J_{C-F} = 245 Hz). Anal. Calcd for $C_{25}H_{16}F_2O_2$: C, 76.99; H, 4.31. Found: C, 76.39; H, 4.31.

Dibenzo[*e,g*]fluoranthene (13a). With stirring under nitrogen at 25 °C, pinacol **12a**[22a] (0.250 g, 0.74 mmol) was added to TfOH (10 mL) and the mixture was stirred for 12 h. After standard workup, and column chromatography with hexanes:ether(19:1), **13a**[23] (0.162 g, 72%) was isolated as a bright yellow crystalline solid.

Acenaphthyleno[1,2-*i*]picene (13d). With stirring under nitrogen at 25 °C, pinacol **12d**[22b] (0.31 g, 0.71 mmol) was added to TfOH (10 mL) and the mixture was stirred for 24 h. After standard workup, and column chromatography with hexane, **13d** (0.110 g, 39%) was isolated as an orange crystalline solid: 306−310 °C; ^{1}H NMR ($CDCl_3$) δ 9.47 (2H, d, J = 7.5 Hz), 8.66 (2H, d, J = 7.2 Hz), 8.57 (2H, d, J = 8.4 Hz), 7.96 (2H, d, J = 7.5 Hz), 7.91 (2H, d, J = 8.7 Hz), 7.78 (2H, d, J = 8.1 Hz), 7.62 (4H, m), 7.46 (2H, m); ^{13}C NMR ($CDCl_3$)[24] δ 138.3, 133.7, 133.0, 131.5, 129.9, 129.6, 129.4, 129.0, 127.8, 127.7, 127.6, 127.2, 127.1, 127.0, 124.7, 124.2, 121.3; HRMS calcd for $C_{32}H_{18}$ 402.1408, found 402.1407.

Dibenzo[*d,h*]crysene (20). To a solution of **18**[26] (0.23 g, 0.64 mmol) in C_6H_6 was added 5 mL of TfOH, and the mixture was stirred at 25 °C for 15 h. The solution was then poured over ice and then extracted into C_6H_6. The organic solution was then washed with 1 M NaOH, brine, and dried with $MgSO_4$. After column chromatography with hexanes:ether (4:1), **20**[27] (0.20 g, 96%) was isolated as a white solid.[27]

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged. We thank Professor Robert Bau at the University of Southern California for his assistance in obtaining the X-ray crystal structure of compound **20**.

Supporting Information Available: Analytical data for compounds **1f**, **1j**, **3f**, **3g**, **3j**, **13a**, **13b**, **13c**, **15**, and **20**. ^{1}H NMR spectra for all products. Synthetic procedures for **13b**, **13c**, and **15** (16 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.

JO970293N

(21) Hatt, H. H. *J. Chem. Soc.* **1929**, 1623.

(22) (a) Acree, S. F. *J. Am. Chem. Soc.* **1912**, *34*, 3687. (b) Moriconi, E. J.; O'Connor, W. F.; Kuhn, L. P.; Keneally, E. A.; Wallenberger, F. T. *J. Am. Chem. Soc.* **1959**, *81*, 6472.

(23) Buchta, E.; Maar, H. *Chem. Ber.* **1962**, *95*, 1826.

(24) Due to low solubility of **13d**, quarternary ^{13}C signals could not be observed.

(25) (a) Trost, B. M. *J. Am. Chem. Soc.* **1966**, *88*, 853. (b) Tatsugi, J.; Okumura, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3311.

(26) Gomberg, M.; Bachmann, W. E. *J. Am. Chem. Soc.* **1927**, *49*, 236.

(27) Dias, J. R. *Handbook of Polycyclic Hydrocarbons*; Elsevier: New York, 1987.