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Working with Hazardous Chemicals

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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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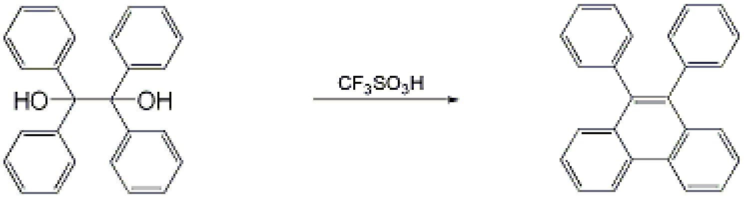
9,10-DIPHENYLPHENANTHRENE

[Phenanthrene, 9,10-diphenyl-]



Submitted by George A. Olah, Douglas A. Klumpp, Donald N. Baek, Gebhart Neyer, and Qi Wang[1] .
Checked by Vladimir Dragan and David J. Hart.

1. Procedure

Caution! Triflic acid is a highly corrosive liquid and should be handled carefully.

9,10-Diphenylphenanthrene . In a 250-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, a thermometer, and a septum is suspended 10.0 g (27.3 mmol) of benzopinacol (Note 1) in 40 mL of dry toluene (Note 2) under a nitrogen atmosphere. The suspension is cooled to 0°C using an ice-acetone bath, and 40 mL of freshly distilled trifluoromethanesulfonic acid (triflic acid) (Note 3) and (Note 4) is added in one portion via syringe (Note 5). The cold bath is removed, and the mixture is stirred for 24 hr at room temperature. The resulting heterogeneous mixture is poured over 100 g of ice, the organic layer is separated, and the aqueous layer is extracted with two 100-mL portions of toluene . The organic layers are combined, and washed with water (50 mL) and with brine (50 mL). The original solution is dried with anhydrous magnesium sulfate , filtered, and the filtrate is concentrated under reduced pressure to afford 9.2 g of crude product (mp 227-231°C) as a pale yellow solid. The crude product is recrystallized from 450 mL of toluene-ethanol (1:1) to give 6.7 g (74%) of pure 9,10-diphenylphenanthrene as a white solid (Note 6). Concentration of the mother liquor and recrystallization of the residue from 100 mL of toluene-ethanol (1:1) gives another 1.4 g (16%) of product (mp 237-238° C).

2. Notes

1. Benzopinacol was purchased from Aldrich Chemical Company, Inc. , and used without further purification.
2. Toluene was purchased from Fisher Scientific Company and distilled from sodium prior to use. Benzene may be substituted for toluene with the following differences: (a) The initial solution is cooled to only 10°C, otherwise the benzene layer freezes. (b) The mixture is extracted with three 100-mL portions of benzene after pouring over ice. (c) Recrystallization from 430 mL of benzene-ethanol (1:1) gives a first crop of pure product in 80-90% yield. The submitters indicate that dichloromethane can be used as the solvent for the reaction and extractions.
3. Triflic acid was obtained from 3M (99% purity). The triflic acid must be distilled prior to its use, and the distillation should be performed under a dry, inert atmosphere. Triflic acid may be recycled using a published procedure.[2]
4. Experiments indicated that the acid strength of the reaction medium must be $H_o = -12$ or stronger. Pure triflic acid has been estimated to be about $H_o = -14$.[3] Contamination of the triflic acid by water results in a weakened acid system. When the acid strength drops below $H_o = -12$, significant quantities of 2,2,2-triphenylacetophenone are produced from the pinacol rearrangement.
5. The temperature of the reaction mixture increases by approximately 15°C during the addition of triflic acid.

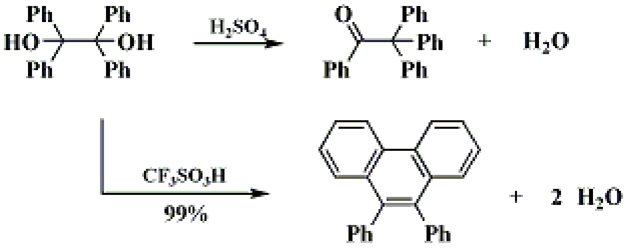
6. This material exhibited the following properties: mp 237-238°C (lit.[4] 238°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.13-7.26 (m, 10 H), 7.5 (t with fine coupling, 2 H, J = 6.9), 7.6 (d with fine coupling, 2 H, J = 8.4), 7.7 (t with fine coupling, 2 H, J = 6.6), 8.82 (d, 2 H, J = 8.1) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 122.9, 126.8, 126.9, 127.1, 128.0, 128.3, 130.4, 131.5, 132.3, 137.6, 139.9 ; HRMS calcd for $C_{26}H_{18}$ 330.1408, found 330.1408 .

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

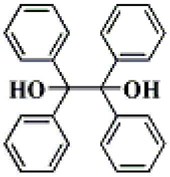
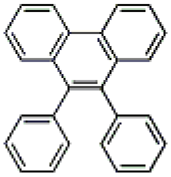
3. Discussion

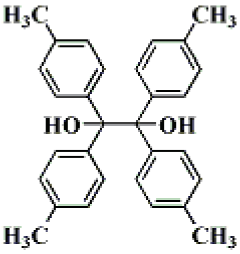
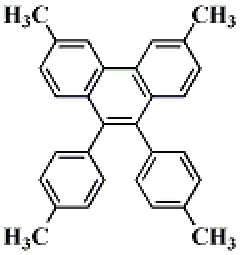
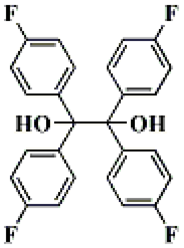
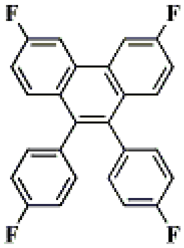
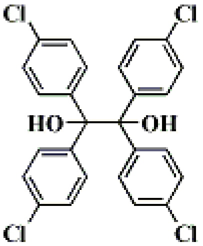
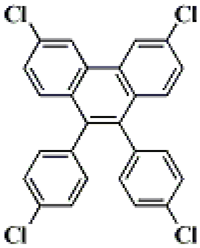
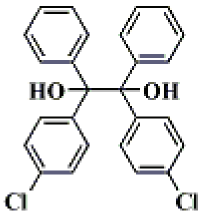
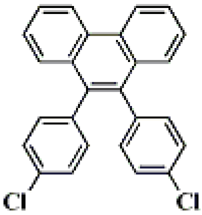
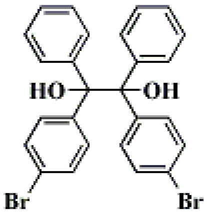
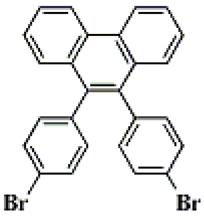
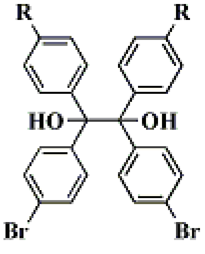
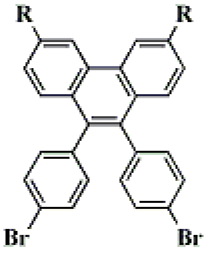
When aromatic pinacols are reacted with an acid, products often arise from dehydration and rearrangement.[5] [6] [7] This general conversion is known as the pinacol rearrangement. The pinacol rearrangement may be promoted by both Brönsted and Lewis acids.[8] [9] In the procedure described here, superacidic triflic acid is reacted with an aryl pinacol and a dehydrative cyclization occurs to give the substituted phenanthrene product. Related to this conversion, the chemistry of benzopinacol in sulfuric acid and triflic acid is contrasted in Scheme 1. We have proposed that the superacidic triflic acid causes the formation of diprotonated intermediates which promote the dehydrative cyclization.[4]



As described in an earlier report,[4] it has been demonstrated that the dehydrative cyclization of aryl pinacols in triflic acid is a general route to substituted phenanthrenes. Some of these conversions are described in the Table. Entries 5-7 show an interesting aspect of the conversion. When two of the aryl rings are substituted by strongly deactivating groups such as chlorine or bromine, the product is formed regioselectively. It may be that the chlorine or bromine deactivate the rings toward cyclization, and that the cyclization is occurring more rapidly through the phenyl or alkylphenyl rings. When two aryl rings are substituted by weakly deactivating groups such as fluorine, poor regiochemistry is observed, and cyclization occurs through both the phenyl and fluorophenyl rings, giving rise to complex product mixtures.

TABLE.
SUBSTITUTED PHENANTHRENES FROM THE DEHYDRATIVE
CYCLICATION OF ARYL PINACOLS IN TRIFIC ACID

Entry	Pinacol	Product	Yield[b]
1			99%
2[a]			90%

			
3[a]			95%
4[a]			100%
5[a]			98%
6[a]			87%
7[a]	 R = $(CH_2)_8CH_3$		94%

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[a] Aryl pinacol prepared by the photolysis of the appropriately substituted benzophenone in isopropyl alcohol.

[b]Yields reported for the crude product.

Aryl pinacols are readily obtained from the photolysis of substituted benzophenones in isopropyl alcohol . Photochemical coupling of benzophenones in isopropyl alcohol has even been reported to occur in direct sunlight.[10] It is known however, that some aryl ketones do not give the pinacol from photolysis in isopropyl alcohol.[11] Nevertheless, aryl pinacols have also been prepared from electrochemical reduction,[12] hydroxylation of olefins,[13] photoreduction of ketones by amines,[14] [15] [16] metal reduction,[17] [18] [19] [20] and by other routes.[21] The phenanthrene ring system has often been prepared by the photochemical cyclization and oxidation of stilbenes,[22] and 9,10-diphenylphenanthrene has been previously synthesized by the reaction of 1,2-dichlorotetraphenylethane with excess aluminum chloride .[23] [24] The present method provides a direct route to substituted phenanthrenes from readily available aryl ketones via the aryl pinacol.

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

9,10-Diphenylphenanthrene:
Phenanthrene, 9,10-diphenyl- (8,9); (602-15-3)

Benzopinacol:
1,2-Ethanediol, 1,1,2,2-tetraphenyl- (8,9); (464-72-2)

Trifluoromethanesulfonic acid: HIGHLY CORROSIVE:
Methanesulfonic acid, trifluoro- (8,9); (1493-13-6)

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