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# Soluble Catalysts for Improved Pschorr Cyclizations[†]

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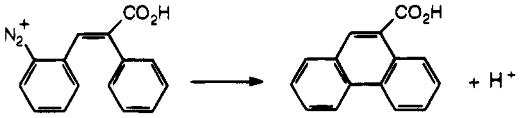
Several improved catalysts for the Pschorr phenanthrene synthesis have been discovered; all are soluble substances which initiate free-radical reactions by electron donation and thereby shorten the reaction time and increase the yield. One technique with $K_4Fe(CN)_6$ in water produced phenanthrene-9-carboxylic acid (**6a**) in 87% yield, but its application did not extend to substituted examples where the diazonium salt is less soluble in water. A more general procedure with ferrocene in acetone produced not only **6a** but also substituted examples **6b−f** in yields of 88−94%. A modification which avoids the isolation of diazonium salts was developed for occasional synthetic use.

## Introduction

The Pschorr reaction,[1] a widely used and reviewed[2] method of synthesis of substituted phenanthroic acids, involves the intramolecular coupling of two aromatic rings through an aryl diazonium salt intermediate. Under traditional reaction conditions, the ring closures of diazonium salts derived from substituted 2-(2-aminophenyl)cinnamic acids (**1** → **2**) were induced by copper or by heating. Cyclization under these conditions required long reaction times (1−24 h) and produced phenanthroic acids in modest but variable yields.[3] Chauncey and Gellert[4] introduced the use of sodium iodide as a soluble catalyst. Yields of cyclization product increased but variability continued to be a problem and significant amounts of iodo substitution products were produced. Later, Elofson and Gadallah[5] electrochemically reduced the diazonium cation and provided additional evidence that the reaction follows a homolytic pathway, first postulated by Waters.[6] Yields were consistently above 80% but the products required a lengthy purification procedure.



**1** **2**

The generally accepted reaction scheme involves the transfer of an electron to the diazonium cation, concomitant loss of a molecule of nitrogen, and formation of an aryl radical which closes upon the adjacent aryl ring.

Catalysts for the Pschorr cyclization and other aryl diazonium salt reactions act as electron donors, and this observation focussed our attention upon discovering more effective catalysts. We have successfully used soluble compounds with low oxidation potentials as catalysts, for example, in Gomberg−Bachmann arylations.[7] In a possible expansion of this principle, we examined the use of soluble catalysts in the free-radical Pschorr cyclization.

## Results

The required cinnamic acids were prepared using Pschorr's original synthetic route (Scheme 1).[1] A Perkin condensation involving *o*-nitrobenzaldehyde and a phenylacetic acid provided a mixture from which the desired isomer **3** was isolated.[2a,8] Ammoniacal ferrous sulfate reduced the nitro group of **3** to provide **4**.[9] The diazonium tetrafluoroborates were prepared by adding a solution of the sodium salt of the amino acid and sodium nitrite to 48% fluoboric acid at 0 °C (**4** → **5**).[10] The solid diazonium tetrafluoroborates were collected and purified by dissolution in anhydrous acetone and reprecipitation with dry ether.[11,12] Tetrafluoroborate salts were used as standards to ensure that yields of ring closure products depended only upon the catalysts and not the diazotization reaction.

We decided in our attempt to catalyze the homolytic reaction that an effective catalyst should have electron donating capability (*i.e.*, low oxidation potential) and should be soluble to eliminate any rate-retarding surface interactions. With this in mind, we studied, in a series of small scale tests, the activity of $SnCl_2$, NaI, $CuSO_4$, $FeSO_4$, $FeSO_4$ in 1 M $H_3PO_4$, $K_4Fe(CN)_6$, and hydroquinone on the ring closure of **5a** in aqueous solution. On the basis of the reaction rate and the purity of the

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[‡] NSF Predoctoral Fellow (1993−present).

[®] Abstract published in *Advance ACS Abstracts*, December 15, 1994.

[1] Pschorr, R. *Ber.* **1896**, *29*, 496.

[2] (a) Fieser, L. F.; Fieser, M. *Natural Products Related to Phenanthrene*, 3rd ed.; Reinhold: New York, 1949; p 8. (b) Leake, P. H. *Chem. Rev.* **1956**, *56*, 27. (c) DeTar, D. F. *Org. React.* **1957**, *9*, 410. (d) Williams, G. H. *Homolytic Aromatic Substitution*; Pergamon: Oxford, 1960; p 80. (e) Abramovitch, R. A. *Adv. Free-Radical Chem.* **1967**, *2*, 87. (f) Kametani, T.; Fukumoto, K. *J. Heterocycl. Chem.* **1971**, *8*, 341. (g) Floyd, A. J.; Dyke, S. F.; Ward, S. E. *Chem. Rev.* **1976**, *76*, 532. (h) Wulfman, D. S. The Chemistry of Diazonium and Diazo Groups. In *The Chemistry of the Functional Groups*; Patai, S., Ed.; Wiley: New York, 1978; pp 276−286. Hegarty, A. F. *Ibid.* 561−564. (i) Saunders, K. H.; Allen, R. L. M. *Aromatic Diazo Compounds*, 3rd ed.; Edward Arnold: London, 1985; p 640.

[3] Pschorr, R.;Tappen, H; Hofmann, R.; Quade, F.; Schütz, M; Popovici, J. *Ber.* **1906**, *39*, 3106.

[4] Chauncey, B.; Gellert, E. *Aust. J. Chem.* **1969**, *22*, 993. Chauncey, B.; Gellert, E. *Aust. J. Chem.* **1970**, *23*, 2503.

[5] Elofson, R. M.; Gadallah, F. F. *J. Org. Chem.* **1971**, *36*, 1769.

[6] Waters, W. A. *Chemistry of Free Radicals*; Oxford Univ. Press: Oxford, 1946.

[7] (a) Pedemonte, R. P. Ph.D. Dissertation, University of Connecticut, 1991. (b) Presented in part at the 193rd American Chemical Society National Meeting, Denver, CO, April, 1987; Abstract ORGN 246. (c) Presented in part at the 197th American Chemical Society National Meeting, Dallas, TX, April, 1990; Abstract ORGN 256.

[8] DeTar, D. F. *Organic Syntheses*; Wiley: New York; 1963; Collect. Vol. 4, p 730.

[9] Bradsher, C. K.; Berger, H. J. *J. Am. Chem. Soc.* **1958**, *80*, 930.

[10] Schofield, K.; Swain, T. *J. Chem. Soc.* **1949**, 2393.

[11] Heacock, R. A.; Hey, D. H. *J. Chem. Soc.* **1952**, 1510.

[12] The diazonium salts exhibited excellent stability and have been stored at 0 °C for over 1 year without significant decomposition.

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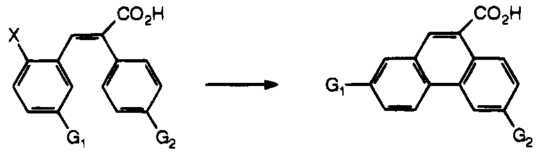
**Scheme 1**



**3**: X = $NO_2$
**4**: X = $NH_2$
**5**: X = $N_2^+$ ($BF_4^-$ or $HSO_4^-$)

**6**

**a**: $G_1 = G_2 = H$ **b**: $G_1 = H, G_2 = OMe$
**c**: $G_1 = H, G_2 = Me$ **d**: $G_1 = H, G_2 = Br$
**e**: $G_1 = H, G_2 = Cl$ **f**: $G_1 = Cl, G_2 = H$

**Table 1. Influence of Catalysts on the Formation of Phenanthrene-9-carboxylic Acid (6a) in Aqueous Solution**

| catalyst | temp (°C) | time[a] | % yield[b] |
|---|---|---|---|
| none | 25 | >56 h | 63 (50) |
| $FeSO_4$ | 25 | >90 min | 59 (49) |
| $FeSO_4$ | 100 | 17 min | 70 (60) |
| $FeSO_4/H_3PO_4$ | 25 | 45 min | 71 (64) |
| $K_4Fe(CN)_6$ | 25 | 45 min | 87 (87)[c] |
| hydroquinone | 25 | 45 min | 84 (81) |

[a] Time required for the complete disappearance of the diazonium salt from the reaction mixture. [b] Yield of purified material in parenthesis. [c] Collected by filtration; product was directly pure.

crude products, it was decided that equimolar amounts of catalyst and diazonium salt gave the best results. Heating the reaction mixtures produced more vigorous nitrogen evolution but the resulting products were contaminated with highly colored side products. Of the catalysts surveyed, the last four gave reasonably clean crude products and were studied further.

The following standard procedure was developed to screen catalysts for the formation of phenanthrene-9-carboxylic acid in aqueous media. An aqueous solution of the diazonium salt **5a** was added dropwise with stirring to an aqueous solution of the catalyst. Reaction times were measured by monitoring the reaction mixture for the disappearance of diazonium salt with 2-naphthol. Failure of a bright red spot to appear indicated that no diazonium salt remained. The product was separated by filtration. The yield and the completion time of the reaction were the major criteria for the judgement of the efficiency of the catalyst. Table 1 summarizes the results of the ring closures of **5a** to **6a** in aqueous solution. Exclusion of all catalysts resulted in a product of poor quality in modest yield and extended the reaction time to over 56 h. The use of catalysts soluble in water reduced the reaction time dramatically and also substantially increased the yield. Hydroquinone and potassium ferrocyanide gave the best yields. Most conveniently, the product of the reaction catalyzed by potassium ferrocyanide was directly pure.

Disappointingly the catalysis by $K_4Fe(CN)_6$ in aqueous media did not extend to substituted examples with equal success. Compound **6f** was obtained in 71% yield; however, examples **6b** and **6c** were produced in low yields (19 and 38%, respectively, of crude material). The low solubility of the substituted diazonium salts in water necessitated working with a slurry and contributed to the poor results. Our inability to develop a completely general procedure in water nevertheless emphasized the desirability of operation with all materials, including the catalysts, in solution.

**Table 2. Influence of Ferrocene on the Formation of Phenanthrene-9-carboxylic Acid (6a) in Acetone**

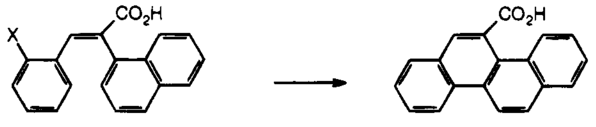
| mol % ferrocene ($Fc/ArN_2^+$) | time[a] | % yield[b] |
|---|---|---|
| 100 | 5 min | 89 |
| 20 | 5 min | 94 |
| 10 | 5 min | 91 |
| 0 | >80 h | 27[c] |

[a] Time required for the complete disappearance of the diazonium salt from the reaction mixture. [b] Isolated yield of pure material after ferrocene was removed in vacuum. [c] The precipitated product obtained in 37% yield was of poor quality and required recrystallization from ethanol.

Rather than pursue operations in water we turned our attention to nonaqueous media. Previous success of the Gomberg–Bachmann arylation in acetone with ferrocene as the homogeneous catalyst prompted us to investigate this system.[7a] In a similar fashion, the diazonium tetrafluoroborate was dissolved in anhydrous acetone and added dropwise with stirring to ferrocene in the same solvent. The first drops turned the solution dark green and caused gas evolution. The reaction was over quickly, and pouring the reaction mixture into water precipitated the product from the solution whose deep blue color was characteristic of ferrocinium ion. The light yellow color of the crude product was due to a small amount of contaminating ferrocene which was effectively removed by sublimation in a vacuum desiccator. Essentially colorless, pure product remained behind in high yield. As expected, the crude product was more highly contaminated where more of the catalyst was used. Routine catalysis with 20 mol % of ferrocene seemed nearly ideal because of a low level of contamination and a consistently high yield. In contrast, when the catalyst was excluded, the reaction required a long time for completion and afforded the product in low yield (Table 2).

The nonaqueous method was successfully extended to the synthesis of substituted phenanthroic acids. Ring closure products **6b–f** were formed in yields ranging from 88 to 94%. In all cases 20 mol % ferrocene was employed except in the case of the bromo acid **6d** where 33 mol % was required to shorten the reaction time and enhance the yield.

Our nonaqueous modification was also successfully extended to the synthesis of chrysene-11-carboxylic acid (**8**). Cyclization onto the naphthyl ring system proceeded quickly, but despite efforts to optimize the reaction conditions, the yield of cyclized product remained about 68%. Although this was lower than that of the other closures, it more than doubled the yield reported earlier.[13]



**7**: X = $N_2^+BF_4^-$

**8**

In order to extend the synthetic usefulness of our method, variations were examined which avoided the isolation of the diazonium salts. Attempts to operate solely in aqueous solutions met with little success, probably because the diazonium sulfates encountered were only slightly soluble; the reactions required more than 1 h to run to completion and the resulting products were highly colored. It was more successful to add

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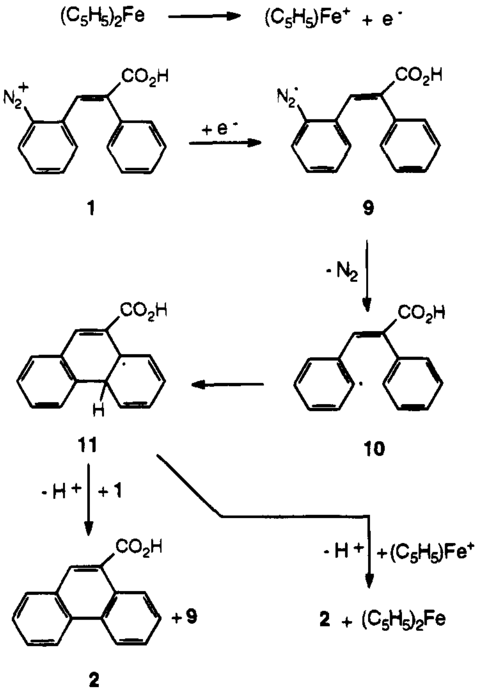
(13) Fieser, L. F.; Joshel, L. M. *J. Am. Chem. Soc.* **1940**, *62*, 1211.

**Scheme 2**



acetone to dissolve the suspension of diazonium sulfates resulting from Pschorr's diazotization method; the resulting homogenous solution was added to ferrocene in acetone. By this method, the yields of **6b** and **6e** were, after recrystallization, 75 and 77%, respectively, based upon the amount of amine starting materials.

## Discussion

Two distinct pathways have been postulated for the Pschorr cyclization. An uncatalyzed thermal reaction is thought to follow a heterolytic $S_N1$ reaction pathway in acid through an aryl cation intermediate.[2c] In contrast, under basic conditions or with copper catalysis in acid, the reaction probably follows a homolytic pathway. Our soluble electron-donors function as important catalysts and their action coincides with the free radical mechanism proposed by a number of others.[6,14] Analogous to related intermolecular diazonium salt decompositions, the catalyst, because of its relatively low oxidation potential, transfers an electron to the diazonium cation **1** (Scheme 2). The resulting diazenyl radical **9** undergoes homolytic bond cleavage to form molecular nitrogen and the aryl radical **10**. The radical then attacks the nearby system and forms the radical intermediate **11**. Loss of an electron and a proton from **11** gives cyclization product **2**. The released electron can either regenerate the original catalyst or add to another diazonium cation to continue the chain.

Our observations are consistent with the free radical mechanism. In the presence of electron-donors, under identical conditions, yields dramatically increase from 27 to 94%, and the reaction times are greatly reduced from 8 h to 5 min. Electron donation by ferrocene was established by the formation of blue ferrocinium ion (oxidized form of the catalyst) during the reaction. Significantly, only 10 mol % of catalyst is needed to improve the reaction markedly. Hence, ferrocene is acting catalytically and promotes a chainlike mechanism. A more subtle, but nonetheless important, observation consonant with a free radical intermediate is the lack of any discernable substituent effect as the groups on the target ring vary from methoxy to chloro. This result parallels Hey and Osbond's findings in the copper-catalyzed reaction.[14c,d]

**Table 3. Potentials of the Catalysts Investigated**

| catalyst with half reaction | potential (E°, V) |
|---|---|
| $Cu^0 \rightarrow Cu^+$ | −0.522 |
| $Cu^+ \rightarrow Cu^{2+}$ | −0.158 |
| $2I^- \rightarrow I_2$ | −0.535 |
| $C_6H_4(OH)_2 \rightarrow C_6H_4O_2$ | −0.6992 |
| $(C_5H_5)_2Fe \rightarrow (C_5H_5)_2Fe^+$ | −0.400 |
| $Fe^{2+} \rightarrow Fe^{3+}$ | −0.771 |
| $Fe^{2+}$ (1 M $H_3PO_4$) $\rightarrow Fe^{3+}$ | −0.438 |
| $[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-}$ | −0.358 |

Success in the Pschorr cyclization has been impeded by the highly reactive natures of both the diazonium salt precursors and their derived radicals. Ionic reactions of diazonium salts compete with the free radical ring closure, while the aryl radical can also be consumed in a number of reactions that do not lead to the cyclization product. Our examination of the Pschorr cyclization uncovered features that limited the success of the reaction. We chose reaction conditions that reduce the competing side reactions and simultaneously enhance the cyclization.

**Catalyst.** In the free radical mechanism, the initiation hinges upon the aquisition of an electron by the diazonium cation. The rate of the reaction is tied to the ease of the electron transfer from the catalyst to the diazonium cation. Our work links the thermodynamic favorability of the electron transfer to the rate that the radical reaction is initiated. Therefore, compounds with low oxidation potentials serve as better catalysts. The major benefit to the reaction is the preferential rate enhancement of the radical ring closure over competing ionic reactions.

In view of the fact that copper acts as an electron donor we looked for soluble compounds with oxidation potentials similar to copper. Table 3 lists the oxidation potentials of our catalysts and some of the previously used compounds.[15] Meaningful comparisons of the effectiveness of the catalysts versus oxidation potential of all the compounds are difficult because of the differences in solubility and reaction media. However, a more limited but nonetheless interesting trend emerged among the iron(II) catalysts in aqueous solution. As the oxidation potential rose from −0.77 through −0.44 to −0.36 for the series $FeSO_4$, $FeSO_4/H_3PO_4$, $K_4Fe(CN)_6$, not only did the reaction rate increase, but also the yield of cyclization product rose from 49 to 87%.

In addition to acting as electron donors, good catalysts should not simultaneously catalyze any side reactions. For example, CuCl serves as an electron donor, but it also fosters the familiar Sandmeyer reaction[16] transforming the diazonium salt into the chlorinated product. Similarly, the iodide ion of NaI, which also possesses a

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[14] (a) Grieve, W. S. M.; Hey, D. H. *J. Chem. Soc.* **1934**, 1797. (b) Hey, D. H.; Waters, W. A. *Chem. Rev.* **1937**, *21*, 169. (c) Hey, D. H.; Osbond, J. M. *J. Chem. Soc.* **1949**, 3164. (d) Hey, D. H.; Osbond, J. M. *J. Chem. Soc.* **1949**, 3172. (e) Lewin, A. H.; Cohen, T. J. *J. Org. Chem.* **1967**, *32*, 3844. (f) Perkins, M. S. In *Free Radicals*; Kochi, J. K., Ed., Wiley: New York, 1973; Vol. 2, p 231.

[15] Hunsberger, J. F. In *Handbook of Chemistry and Physics*, 63rd ed.; Weast, R. C., Ed., CRC Press: New York, 1982; pp 162–167.

[16] March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 647.

low oxidation potential, consistently leads to the formation of roughly 10% of the iodination product.[4,17]

The solubility of the catalyst in the reaction medium is a factor in the efficiency of the reaction. Pschorr employed copper powder in aqueous acidic solution as a heterogeneous catalyst for the formation of phenanthroic acid. As the soluble diazonium salt cyclized, the product precipitated upon the surface of the copper metal and both reduced the effective area of the catalyst and lowered the efficiency of electron transfer. Our solution to this problem was to use soluble catalysts; their use provided consistently beneficial results.

**Temperature.** The diazonium salts used in the Pschorr cyclization are thermally labile and undergo heterolytic bond cleavage to form nitrogen and aryl cations. In water, the cations form phenols (eq 1). This

$$\mathrm{ArN_2}^+ \xrightarrow{-\mathrm{N_2}} \mathrm{Ar}^+ \xrightarrow{\mathrm{H_2O}} \mathrm{ArOH} + \mathrm{H}^+ \qquad (1)$$

side reaction becomes a major competitor to the cyclization when the reaction is run at higher temperatures.[2b,c] As we noted in our initial aqueous catalyst screenings, heating the reaction solutions produced brightly colored solids. These are likely azo byproducts; one type is produced in a coupling reaction between the diazonium salt and activated phenolic rings (eq 2).[18] Because of

$$\mathrm{ArN{=}N}^+ + \mathrm{Ar'OH} \rightarrow \mathrm{ArN{=}NAr'OH} + \mathrm{H}^+ \qquad (2)$$

these competing thermal reactions, we sought catalysts that efficiently promoted the radical reaction at ambient temperature.

**Order of Addition.** Traditionally, the catalyst is added all at once to the diazonium salt solution. This procedure generates aryl radicals in a highly concentrated diazonium cation solution and fosters formation of another type of azo compound. Minisci has found that under reductive conditions diazo coupling of diazonium salts and aryl radicals occurs readily (eqs 3 and 4).[19] By

$$\mathrm{ArN{=}N}^+ + \dot{\mathrm{A}}\mathrm{r}' \rightarrow [\mathrm{ArN{=}NAr'}]^{\bullet +} \qquad (3)$$

$$[\mathrm{ArN{=}NAr'}]^{\bullet +} + \mathrm{Fe}^{2+} \rightarrow \mathrm{ArN{=}NAr'} + \mathrm{Fe}^{3+} \qquad (4)$$

reversing the usual order of addition, we have suppressed the problem and achieved high yields.

**Solvent.** We have already commented that low solubilities of product and catalyst in the reaction solvent seem to lower the efficiency of the Pschorr cyclization. Likewise, we observed that poor solubility of the diazonium salt depresses yields. We sought better polar solvents for starting materials, catalysts, and products. Commonly used solvents that are susceptible to free radical hydrogen or halogen abstractions such as primary and secondary alcohols, ethers, and halogenated solvents were avoided. Acetone proved to be the solvent of choice because it is relatively inert, readily available, and inexpensive.

## Conclusions

In our exploration of the Pschorr cyclization, we have discovered a number of readily available soluble electron-donating compounds that act as efficient catalysts. This discovery enabled us to improve the synthesis of substituted phenanthroic acids. In aqueous media, hydroquinone and potassium ferrocyanide emerged as superior catalysts in the formation of phenanthrene-9-carboxylic acid (**6a**) which results in 84–87% yield from the diazonium tetrafluoroborate within 45 min. Unfortunately, however, the improvements expected from this method did not extend to substituted phenanthroic acids. A more general technique we developed involved operation in acetone where ferrocene was a very effective catalyst. Importantly this method rapidly provided not only **6a** but also the substituted examples **6b–g** (in yields of 88–94%). A modification of the general method was developed to avoid isolation of the diazonium salt intermediate. In these cases the amine was diazotized in aqueous solution and any precipitated salt was redissolved by the addition of acetone. The cyclization was quickly completed by the addition of this solution to ferrocene in acetone. Overall yields for two substituted examples (**6b** and **6e**) were 75–77%. These improvements of the Pschorr cyclization convert it into a reliable and powerful synthetic method.

## Experimental Section

**General.** Melting points are uncorrected.

**(*E*)-3-(2-Nitrophenyl)-2-phenyl-2-propenoic Acid (3a).** This compound was prepared by a standard Perkin condensation of 2-nitrobenzaldehyde with a phenylacetic acid.[1] In a 250-mL three-neck flask equipped with a magnetic stirrer and a condenser were combined 7.95 g (0.053 mol) of 2-nitrobenzaldehyde, 10.40 g (0.076 mol) of phenylacetic acid, 27.10 g (0.265 mol) of acetic anhydride, and 5.36 g (0.053 mol) of triethylamine. The solution was boiled under reflux for 15 min, cooled to 90 °C, and diluted with 25 mL of water over a 5 min period while maintaining the temperature between 90–100 °C. The solution was cooled slowly to between 0–5 °C and 10.82 g (76%) of a crude red solid was collected. The crude product was recrystallized from toluene and gave 8.80 g (62%) of yellow needles; mp 197.5–198.5 °C (lit.[2] mp 197.8–198.3 °C); IR (KBr) 3100–2500 ($\mathrm{CO_2H}$), 1685 (C=O), 1519 and 1338 ($\mathrm{NO_2}$), 746 (1,2-$\mathrm{C_6H_4}$), 710 cm$^{-1}$ ($\mathrm{C_6H_5}$); $^1$H NMR (60 MHz, acetone-$d_6$) 8.1–6.7 (m).

The following were prepared similarly:

**(*E*)-2-(4-Methoxyphenyl)-3-(2-nitrophenyl)-2-propenoic acid (3b)** from 2-nitrobenzaldehyde and of 4-methoxyphenylacetic acid in 53% yield; light yellow crystals (from toluene); mp 175–176 °C (lit.[20] mp 177 °C); IR (KBr) 3100–2500 ($\mathrm{CO_2H}$), 1684 (C=O), 1517 and 1365 ($\mathrm{NO_2}$), 1253 (C–O), 832 cm$^{-1}$ (1,4-$\mathrm{C_6H_4}$); $^1$H NMR (60 MHz, acetone-$d_6$) 8.1–6.7 (9H, m), 3.7 (3H, s).

**(*E*)-2-(4-Methylphenyl)-3-(2-nitrophenyl)-2-propenoic acid (3c)** from 2-nitrobenzaldehyde and 4-methylphenylacetic acid in 56% yield; yellow crystals (from 95% ethanol); mp 208–210 °C (lit.[3] mp 211 °C); IR (KBr) 3100–2500 ($\mathrm{CO_2H}$), 1684 (C=O), 1518 and 1340 ($\mathrm{NO_2}$), 823 (1,4-$\mathrm{C_6H_4}$), 732 cm$^{-1}$ (1,2-$\mathrm{C_6H_4}$); $^1$H NMR (60 MHz, acetone-$d_6$) 8.1–6.7 (9H, m), 2.3 (3H, s).

**(*E*)-2-(4-Bromophenyl)-3-(2-nitrophenyl)-2-propenoic acid (3d)** from 2-nitrobenzaldehyde and 4-bromophenylacetic acid in 28% yield; yellow cubes (from toluene); mp 178–179 °C (lit.[3] mp 187 °C); IR (KBr) 3100–2500 ($\mathrm{CO_2H}$), 1687 (C=O), 1517 and 1338 ($\mathrm{NO_2}$), 827 (1,4-$\mathrm{C_6H_4}$), 744 cm$^{-1}$ (1,2-$\mathrm{C_6H_4}$); $^1$H NMR (60 MHz, acetone-$d_6$) 8.1–6.7 (m).

**(*E*)-2-(4-Chlorophenyl)-3-(2-nitrophenyl)-2-propenoic acid (3e)** from 2-nitrobenzaldehyde and 4-chlorophenylacetic acid in 43% yield; yellow cubes; mp 186–187 °C (lit.[21] mp 186–186.5 °C); IR (KBr) 3100–2500 ($\mathrm{CO_2H}$), 1686 (C=O),

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(17) Foldeak, S. *Tetrahedron* **1971**, *27*, 3465. Buckley, T. F.; Rapoport, H. *J. Org. Chem.* **1983**, *48*, 4222. Duclos, R. I.; Tung, J. S.; Rapoport, H. *J. Org. Chem.* **1984**, *49*, 5243.

(18) Griess, P. *Ann.* **1866**, *137*, 85. Liebermann, C. *Ber.* **1883**, *16*, 2853.

(19) Minisci, F.; Coppa, F.; Fontana, F.; Pianese, G.; Zhao, L. *J. Org. Chem.* **1992**, *57*, 3929.

(20) Pschorr, R; Wolfes, O.; Buckom, W. *Ber.* **1900**, *33*, 162.

1519 and 1341 ($NO_2$), 826 cm$^{-1}$ (1,4-$C_6H_4$); $^1$H NMR (60 MHz, acetone-$d_6$) 8.1–6.7 (m).

**(*E*)-3-(2-Aminophenyl)-2-(phenyl)-2-propenoic acid (4a).** This compound was prepared by a standard reduction with an ammoniacal suspension of ferrous hydroxide.[1] A solution of 8.40 g (31.2 mmol) of **3a** in 400 mL of 10% $NH_4OH$ was added to a boiling mixture of 61.17 g (205.9 mmol) of $FeSO_4{\cdot}7H_2O$, 400 mL of water, and 450 mL of concd $NH_4OH$. The mixture was boiled for 15 min and filtered. The filtrate was neutralized with acetic acid. The light yellow product was recrystallized from toluene to give 6.37 g (86%) of yellow cubes; mp 186–187 °C (lit.[1] mp 185–186 °C); IR (KBr) 3396 (N–H), 1686 (C=O), 746 cm$^{-1}$ (1,2-$C_6H_4$); $^1$H NMR (60 MHz, acetone-$d_6$) 7.7–6.6 (m).

The following were prepared similarly:

**(*E*)-3-(2-Aminophenyl)-2-(4-methoxyphenyl)-2-propenoic acid (4b)** in 85% yield; yellow cubes (from toluene); mp 149–150 °C (lit.[20] mp 149 °C); IR (KBr) 2938–2550 ($NH_3^+$), 1600 ($CO_2^-$), 837 (1,4-$C_6H_4$), 747 cm$^{-1}$ (1,2-$C_6H_4$); $^1$H NMR (60 MHz, acetone-$d_6$) 7.8–6.0 (9H, m), 3.7 (3H, s).

**(*E*)-3-(2-Aminophenyl)-2-(4-methylphenyl)-2-propenoic acid (4c)** in 96% yield; white needles (from 66% ethanol); mp 205–206 °C (lit.[3] mp 206 °C); IR (KBr) 3020–2658 ($NH_3^+$), 1600 ($CO_2^-$), 818 (1,4-$C_6H_4$), 744 cm$^{-1}$ (1,2-$C_6H_4$); $^1$H NMR (60 MHz, acetone-$d_6$) 7.8–6.0 (9H, m), 2.2 (3H, s).

**(*E*)-3-(2-Aminophenyl)-2-(4-bromophenyl)-2-propenoic acid (4d)** in 66% yield; white needles (from (1:10) acetic acid–toluene); mp 224.5–225.5 °C (lit.[3] mp 222–223 °C); IR (KBr) 2936–2600 ($NH_3^+$), 1600 ($CO_2^-$), 829 (1,4-$C_6H_4$), 743 cm$^{-1}$ (1,2-$C_6H_4$); $^1$H NMR (60 MHz, acetone-$d_6$) 7.8–6.0 (m).

**(*E*)-3-(2-Aminophenyl)-2-(4-chlorophenyl)-2-propenoic acid (4e)** in 76% yield; white needles (from (1:10) acetic acid–toluene); mp 226–227 °C (lit.[21] mp 224 °C); IR (KBr) 2944–2650 ($NH_3^+$), 1600 ($CO_2^-$), 832 (1,4-$C_6H_4$), 743 cm$^{-1}$ (1,2-$C_6H_4$); $^1$H NMR (60 MHz, acetone-$d_6$) 7.8–7.1 (m).

**(*E*)-2-(1-Naphthyl)-3(2-nitrophenyl)-2-propenoic Acid and (*E*)-3-(2-Aminophenyl)-2-(1-naphthyl)-2-propenoic Acid.** These compounds, prepared by literature methods on similar scales with similar yields, showed the literature melting points.[13]

**(*E*)-2-(2-Carboxy-2-phenylethenyl)benzenediazonium Tetrafluoroborate (5a).** This compound was prepared by a modified procedure for diazotization of aromatic amines with subsequent tetrafluoroborate salt formation.[10] A solution composed of 1.00 g (4.2 mmol) of **4a**, 0.18 g (4.6 mmol) of NaOH, and 0.30 g (4.2 mmol) of $NaNO_2$ in 10 mL of water was added dropwise over 20 min with stirring to 10.60 g (60 mmol) of 50% fluoboric acid at 0–5 °C. During the addition, a solid precipitated; after 50 min of additional stirring, sulfamic acid was added until the mixture tested negative to starch-iodide paper. The crude yellow solid collected was then dissolved in the smallest amount of acetone; the solution was chilled to about 0–5 °C and cold anhydrous ether was added to precipitate 1.168 g (83%) of the yellow diazonium salt; mp 106 °C dec; IR (KBr) 2269 ($N_2^+$), 772 (1,2-$C_6H_4$), 702 cm$^{-1}$ ($C_6H_5$). Anal. Calcd for $C_{15}H_{11}BF_4N_2O_2$: C, 53.29; H, 3.28; N, 8.29. Found: C, 53.09; H, 3.16; N, 8.44.

The following were prepared similarly:

**(*E*)-2-(2-Carboxy-2-(4-methylphenyl)ethenyl)benzenediazonium tetrafluoroborate (5c)** in 72% yield; yellow salt; mp 116 °C dec after whitening at 113–116 °C; IR (KBr) 2243 ($N_2^+$), 830 (1,4-$C_6H_4$), 770 cm$^{-1}$ (1,2-$C_6H_4$). Anal. Calcd for $C_{16}H_{13}BF_4N_2O_2$: C, 54.58; H, 3.72; N, 7.96. Found: C, 54.36; H, 3.57; N, 8.15.

**(*E*)-2-(2-Carboxy-2-(4-bromophenyl)ethenyl)benzenediazonium tetrafluoroborate (5d)** in 72% yield; yellow salt; mp 174 °C dec after whitening at 117 °C; IR (KBr) 2271 ($N_2^+$), 834 (1,4-$C_6H_4$), 762 cm$^{-1}$ (1,2-$C_6H_4$). Anal. Calcd for $C_{15}H_{10}BBrF_4N_2O_2$: C, 43.21; H, 2.42; N, 6.72. Found: C, 43.06; H, 2.39; N, 6.44.

**(*E*)-2-(2-Carboxy-2-(4-chlorophenyl)ethenyl)benzenediazonium tetrafluoroborate (5e)** in 56% yield; yellow salt; mp 181 °C dec after whitening at 114–115 °C; IR (KBr) 2271 ($N_2^+$), 838 (1,4-$C_6H_4$), 767 cm$^{-1}$ (1,2-$C_6H_4$). Anal. Calcd for $C_{15}H_{10}BClF_4N_2O_2$: C, 48.36; H, 2.71; N, 7.52. Found: C, 48.19; H, 2.60; N, 7.79.

**(*E*)-2-(2-Carboxy-2-(2-chlorophenyl)ethenyl)benzenediazonium tetrafluoroborate (5f)** in 55% yield; yellow salt; mp 158 °C dec; IR (KBr) 2275 ($N_2^+$), 700 cm$^{-1}$ ($C_6H_5$). Anal. Calcd for $C_{15}H_{10}BClF_4N_2O_2$: C, 48.36; H, 2.71; N, 7.52. Found: C, 48.21; H, 2.63; N, 7.75.

**(*E*)-2-(2-Carboxy-2-(1-naphthyl)ethenyl)benzenediazonium tetrafluoroborate (7)** in 67% yield; yellow salt; mp 109–110 °C dec; IR (KBr) 2271 cm$^{-1}$ ($N_2^+$). Anal. Calcd for $C_{19}H_{13}BF_4N_2O_2$: C, 58.79; H, 3.38; N, 7.22. Found: C, 58.50; H, 3.24; N, 6.89.

**(*E*)-2-(2-Carboxy-2-(4-methoxyphenyl)ethenyl)benzenediazonium Tetrafluoroborate (5b).** This diazonium salt was prepared in a manner similar to the others except 5.49 g (20.0 mmol) of **4b** was first added to 50 mL of 6.0 M HCl, followed by heating to 100 °C and rapid cooling to 0 °C. A solution composed of 1.60 g (23.0 mmol) of $NaNO_2$ in 6 mL of water was added dropwise over 20 min with stirring to the amino acid–HCl suspension, at 0–5 °C. After 10 min of additional stirring, sulfamic acid was added until the mixture tested negative to starch–iodide paper. The diazonium salt mixture was then dissolved in 175 mL of water and was filtered by gravity. While the solution was being stirred in an ice bath, 7.32 g (40.0 mmol) of fluoboric acid was added dropwise. The yellow diazonium salt was collected and purified using the acetone/ether method to give 2.67 g (36%); mp 115 °C dec; IR (KBr) 2274 ($N_2^+$), 834 (1,4-$C_6H_4$), 776 cm$^{-1}$ (1,2-$C_6H_4$). Anal. Calcd for $C_{16}H_{13}BF_4N_2O_3$: C, 52.21; H, 3.56; N, 7.61. Found: C, 52.06; H, 3.46; N, 7.47.

**Phenanthrene-9-carboxylic Acid (6a) Preparation in Nonaqueous Medium.** Compound **5a** (0.50 g, 1.5 mmol) was dissolved in 25 mL of anhydrous acetone and added dropwise with stirring over a 5 min period to 0.056 g (0.3 mmol) of ferrocene in 5 mL of acetone at room temperature. After an additional 5 min of stirring the 2-naphthol test was negative and the green reaction mixture was added to 70 mL of water. A light yellow precipitate was collected and placed in a vacuum desiccator overnight to remove trace amounts of ferrocene; 0.314 g (94%) of a white solid was recovered; mp 256–257 °C (lit.[1] mp 256–257 °C); IR (KBr) 1685 cm$^{-1}$ (C=O); $^1$H NMR (270 MHz, DMSO-$d_6$) 7.6–8.8 (m).

The reaction was performed as above except for the omission of the catalyst; it required more than 80 h to give a negative 2-naphthol test and yielded 0.090 g (27%) of **6a**.

**6-Methoxyphenanthrene-9-carboxylic acid (6b)** was prepared by the model procedure using 0.50 g (1.4 mmol) of **5b** and 0.056 g (0.30 mmol) of ferrocene. The white solid was collected and placed in a vacuum desiccator overnight to give 0.311 g (88%) of a white solid; mp 239.5–240.5 °C (lit.[20] mp 239 °C); IR (KBr) 1681 (C=O), 1230 cm$^{-1}$ (C–O); $^1$H NMR (270 MHz, DMSO-$d_6$) 7.6–8.9 (8H, m), 4.1 (3H, s).

**6-Methylphenanthrene-9-carboxylic Acid (6c).** Prepared by the model procedure using 0.50 g (1.4 mmol) of **5c** and 0.052 g (0.28 mmol) of ferrocene. The white solid was collected and placed in a vacuum desiccator overnight and heated in a drying oven for 2 min at 140 °C to give 0.296 g (89%) of a white solid; mp 236–238 °C (lit.[3] mp 238 °C); IR (KBr) 1687 cm$^{-1}$ (C=O); $^1$H NMR (270 MHz, DMSO-$d_6$) 7.4–8.9 (8H, m), 2.1 (3H, s).

**6-Bromophenanthrene-9-carboxylic acid (6d)** was prepared by the model procedure using 0.50 g (1.1 mmol) of **5d** and 0.069 g (0.37 mmol) of ferrocene. The white solid was collected and placed in a vacuum desiccator overnight and recrystallized from 95% ethanol to give 0.258 g (89%) of a white solid; mp 297–298 °C (lit.[3] mp 290–291 °C); IR (KBr) 1679 cm$^{-1}$ (C=O); $^1$H NMR (270 MHz, DMSO-$d_6$) 7.66–9.08 (m).

**6-Chlorophenanthrene-9-carboxylic acid (6e)** was prepared by the model procedure using 0.50 g (1.3 mmol) of **5e** and 0.056 g (0.30 mmol) of ferrocene. The light pink product was collected and placed in a vacuum desiccator overnight and then oven dried at 140 °C for 3 min yielding 0.298 g (94%) of a white solid; mp 301–303 °C (lit.[21] mp 301.5–302.5 °C); IR (KBr) 1679 cm$^{-1}$ (C=O); $^1$H NMR (270 MHz, DMSO-$d_6$) 7.67–8.94 (m).

**2-Chlorophenanthrene-9-carboxylic acid (6f)** was prepared by the model procedure using 0.50 g (1.3 mmol) of **5f** and 0.056 g (0.30 mmol) of ferrocene. The white solid was collected and placed in a vacuum desiccator overnight to give 0.306 g (92%) of a white solid; mp 240–242 °C (lit.[10] mp 233–234 °C); IR (KBr) 1715 cm$^{-1}$ (C=O); $^1$H NMR (270 MHz, DMSO-$d_6$) 7.66–9.08 (m).

**Chrysene-11-carboxylic acid (8)** was prepared by the model procedure using 0.394 g (1.0 mmol) of **7** and 0.038 g (0.20 mmol) of ferrocene. The buff colored product was collected and placed in a vacuum desiccator overnight yielding 0.188 g (68%) of a solid; mp 219.5–221.5 °C dec (lit.[13] mp 225–226 °C dec); IR (KBr) 1686 cm$^{-1}$ (C=O).

**Phenanthrene-9-carboxylic Acid (6a). Preparation in Aqueous Solution.** Compound **5a** (0.50 g, 1.5 mmol) was dissolved in 50 mL of water. In a separate flask, 0.634 g (1.5 mmol) of $K_4Fe(CN)_6{\cdot}3H_2O$ was dissolved in 50 mL of water. At room temperature, the diazonium salt solution was added dropwise with stirring over a 30-min period to the $K_4Fe(CN)_6{\cdot}3H_2O$ solution. After an additional 15 min of stirring, the 2-naphthol test was negative; a slightly pink solid was collected and placed in a vacuum desiccator overnight to dry; 0.288 g (87%) of a pure white solid was recovered; mp 256–257 °C (lit.[1] mp 256–257 °C). When the reaction was repeated except for the omission of the catalyst it required more than 56 h to give a negative 2-naphthol test and after recrystallization from 95% ethanol gave 0.167 g (50%) of product.

The above procedure using $K_4Fe(CN)_6{\cdot}3H_2O$ was also followed for the preparation of phenanthroic acids **6b**, **6c**, and **6f**. These materials were produced, respectively, in yields of 71% (after sublimation), 19% (crude), and 38% (crude).

The above procedure was used to screen catalysts in the preparation of phenanthroic acid: Equimolar amounts of $FeSO_4$ at 25 and 100 °C gave **6a** in 59 and 70% yields, respectively. Yields of these products purified by recrystallization from 95% ethanol were 49 and 60%, respectively. The same procedure with equimolar amounts of $FeSO_4$ in 1 M $H_3PO_4$ or of hydroquinone gave **6a** in 71 and 84% yields, respectively. Yields of these products, after purification by sublimation, were 64 and 81%, respectively.

**6-Chlorophenanthrene-9-carboxylic Acid (6e). Preparation without Isolation of the Diazonium Salt.** Compound **4e** (0.50 g, 1.83 mmol) was dissolved in a solution containing NaOH (0.091 g, 2.3 mmol), $NaNO_2$ (0.147 g, 2.1 mmol), and 8 mL of water. The solution was then added dropwise over a 15-min period with stirring to sulfuric acid (2.150 g, 21.9 mmol) in 8 mL of water at 0 °C. The solution was stirred for an additional 25 min and excess nitrous acid was destroyed by adding sulfamic acid. Acetone (12 mL) was added to the suspension and the resulting solution was added dropwise over a 5-min period with stirring to a solution of ferrocene (0.068 g, 0.37 mmol) in 5 mL of acetone. Immediately at the end of the addition, the reaction mixture was negative to the 2-naphthol test and was added to 40 mL of water. The deep peach-colored solid was recovered by suction filtration and recrystallized from ethanol–water to give 0.358 g (77%) of a white product; mp 299.5–300.5 °C (lit.[21] mp 301.5–302.5 °C).

**6-Methoxyphenanthrene-9-carboxylic Acid (6b). Preparation without Isolation of the Diazonium Salt.** The same procedure was used as above from compound **4b** in 75% yield; white solid; mp 238.5–239.5 °C (lit.[20] mp 239 °C).

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