case such experiments, combined with the specific nature of the transformation involved, have allowed us to delineate especially sharply the mechanism of a carbon-carbon bond-forming reaction mediated by a binuclear organotransition metal complex.

Acknowledgment. We are grateful to Mr. William D. Jones and Mr. Rudi Nunlist for assistance in obtaining 180-MHz FT NMR spectra and to Dr. Arnold Falick and Ms. Sherry Ogden for obtaining mass spectral data. We are also grateful to the National Science Foundation (Grant No. CHE78-08706) and the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. W-7405-Eng.-48, for financial support.

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(5) Allowing **8** to react with excess PPh_3 under the reaction conditions (sealed tube) yielded the complex analogous to **8** having the $Co(CO)_2$ group replaced by a $Co(CO)(PPh_3)$ group.
(6) An alternative possibility involves methyl transfer from D to a second molecule of **7**, initiating a chain process of the type suggested in ref 1. We cannot rigorously rule out this process; however, no evidence for this type of autocatalysis was evident in our kinetics experiments.
(7) Hertz Foundation Fellow, 1977–present.
(8) Note Added in Proof. A binuclear intermediate very similar to C, also containing a single carbonyl bridge but no metal-metal bond, was observed recently in a study of photosubstitution of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$: Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2753.

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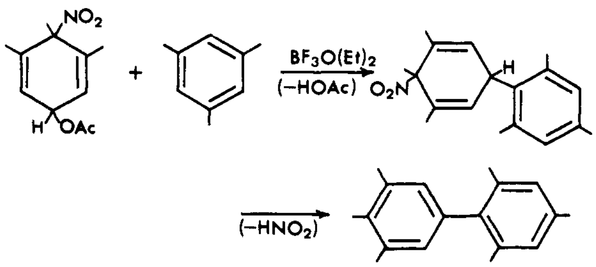
Ipso Nitration. Use of Ipso Nitration Products as Sources of Carbon Electrophiles in Regiospecific Syntheses of Aromatic Derivatives

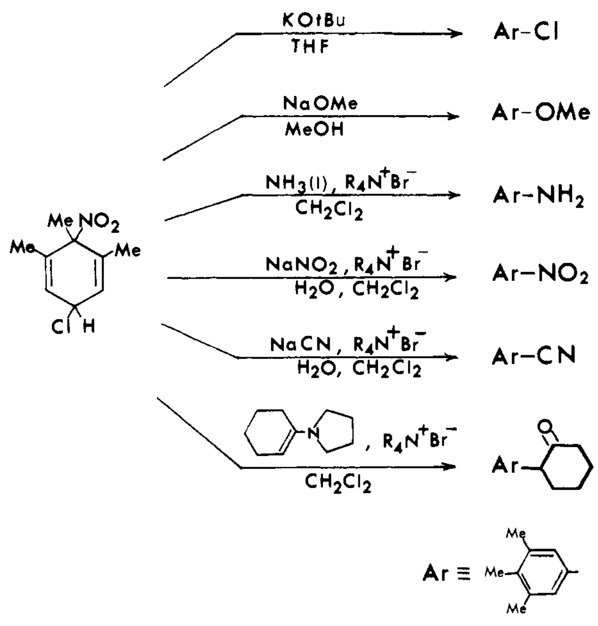
Sir:

Ipso nitration products can be used under conditions of acid catalysis to mount electrophilic substitutions on reactive aromatics.[1-3] The general pattern is exemplified by reaction of 4-nitro-3,4,5-trimethylcyclohexadienyl acetate (**1**) with mesitylene in the presence of boron trifluoride etherate to give the hexamethylbiphenyl derivative in better than 90% yield (eq 1). The more general use of these derivatives as sources of carbon electrophiles requires conversion of the acetate function into a leaving group that does not require strong acid media for activation. One obvious strategy is the conversion of nitrodienyl acetates into nitrodienyl halides. We report here convenient ways to accomplish such transformations and demonstrate the utility of nitrodienyl halides, formal 1,4-adducts of nitryl halides and aromatic, in regiospecific syntheses of a range of aromatic derivatives.



(1)

Scheme I



Compound **1** was readily converted into 4-nitro-3,4,5-trimethylcyclohexadienyl chloride (**2**) by passing a stream of hydrogen chloride through a suspension of **1** in pentane-ether (10:1) for 5 min at −10 °C followed by an additional 5-min reaction period at the same temperature.[4] Colorless, crystalline **2** was isolated in quantitative yield by vacuum evaporation of the solvents and the acetic acid byproduct, mp 61–62 °C dec.[5] Thermal decomposition of **2** at 200 °C yields mainly 1,2,3-trimethylbenzene plus some 5-chloro-1,2,3-trimethylbenzene and 4-nitro-1,2,3-trimethylbenzene. Spectral studies indicate that **2** has a half-life of <60 s upon solvolysis in 50% ethanol,[6] and product studies reveal both 5-hydroxy- and 5-ethoxy-1,2,3-trimethylbenzene with <1% of the 5-chloro derivative. Reaction of **2** in methanolic sodium methoxide gave 5-methoxy-1,2,3-trimethylbenzene in >90% yield with trace amounts of the 5-chloro derivative. Reaction of **2** with potassium *tert*-butoxide in tetrahydrofuran gave 5-chloro-1,2,3-trimethylbenzene in 85% yield.

Treatment of methylene chloride solutions of **2** with liquid ammonia gave no significant yield of 5-amino-1,2,3-trimethylbenzene, but, upon addition of tetrabutylammonium bromide to the same reaction mixture, a 78% yield of the 5-amino derivative was obtained. The reaction of a stirred solution of **2** (0.16 M) in methylene chloride with an aqueous solution of sodium nitrite (3.5 M) and tetrabutylammonium bromide (2.5 M) at 0 °C for 6 h gave a 60% yield of 5-nitro-1,2,3-trimethylbenzene. Similarly, the reaction of **2** in methylene chloride with aqueous sodium cyanide and tetrabutylammonium bromide gave 5-cyano-1,2,3-trimethylbenzene in 75% yield. Finally, reaction of **2** with the pyrrolidine enamine of cyclohexanone and tetrabutylammonium bromide gave, after acid hydrolysis, a 50% yield of 5-(2-cyclohexanoyl)-1,2,3-trimethylbenzene. These results are summarized in Scheme I.[7,8]

We have been unable to convert 4-methyl-4-nitrocyclohexadienyl acetate into the corresponding nitrodienyl chloride, but reaction with hydrogen bromide proceeds readily to yield the labile nitrodienyl bromide. Direct reaction of crude preparations of this nitrodienyl bromide in methylene chloride with aqueous sodium nitrite and tetrabutylammonium bromide gives *p*-nitrotoluene in 60% yield, based on nitrodienyl bromide, with no detectable *o*-nitrotoluene.

The loss of nitrite from **1** in aqueous solvents is known to be facile. Strong acid catalysis is required for the departure of

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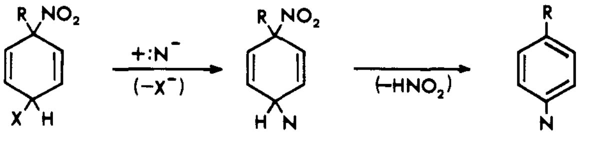
acetate to be competitive with the departure of nitrite.[9,10] The situation is clearly quite different with **2**, where the product data from aqueous solvolysis show that displacement of halogen occurs before loss of nitrite and subsequent rearomatization. With sufficiently hindered bases, such as *tert*-butoxide ion, it is possible to retain the halogen and promote what we presume to be an E2 elimination of the elements of nitrous acid. Within reasonable steric contraints, however, displacement prior to elimination may be anticipated as indicated in eq 2.



(2)

Rates of displacement are significantly enhanced by transforming the nitrodienyl chloride (**2**) to the nitrodienyl bromide in situ with the use of tetrabutylammonium bromide. The tetrabutylammonium cation also facilitates phase transfer of anions such as cyanide and nitrite, making it possible to conduct efficient displacement-elimination sequences in two-phase reaction mixtures.

It should not pass unnoticed that regiospecific nitration is now possible. One can direct the course of reaction of an ipso nitration product so that either the isomerically pure *o*-nitroalkylbenzene *or* the *p*-nitroalkylbenzene may be obtained from the same starting material. Thus treatment of 4-methyl-4-nitrocyclohexadienyl acetate with concentrated sulfuric acid yields *o*-nitrotoluene, but the sequence of displacements and elimination described above yields the para isomer. The utility of these reactions is enhanced by the development of efficient syntheses of 4-alkyl-4-nitrocyclohexadienyl acetates.[11]

The ease with which all of these transformations may be conducted and the apparent versatility of the general reaction sequence deserves stress. Ipso nitration products, curiosities uncovered by detailed mechanistic studies of aromatic nitration, appear to have significant synthetic potential.[12]

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(4) The suspended sample of 1 dissolves during the addition of hydrogen chloride to yield a clear, colorless solution. The same product is obtained from either (*Z*)-**1** (mp 118–119 °C) or (*E*)-**1** (mp 65–66 °C). Reconversion of **2** into **1** by treatment of **2** with silver acetate gave a mixture of (*Z*)-**1** and (*E*)-**1**.
(5) ^{1}H NMR (DCCl$_3$): δ 1.78 (m, 9 H, methyl), 5.04 (m, 1 H, methine), 5.97 (m, 2 H, vinyl); decoupling of the methyl protons resulted in a triplet for the methine signal and a doublet for the vinyl protons, $J = 4.3$ Hz.
(6) The half-life of **2** in aqueous ethanol is about that found for 4-nitro-3,4,5-trimethylcyclohexadienol; see K. S. Feldman, A. McDermott, and P. C. Myhre. *J. Am. Chem. Soc.*, **101**, 505 (1979).
(7) Satisfactory analytical and spectral data were obtained for all compounds reported.
(8) In initial studies, 4-nitro-3,4,5-trimethylcyclohexadienyl bromide was prepared by reaction of **1** in methylene chloride with boron trifluoride and tetrabutylammonium bromide at −78 °C. The resulting solution was treated with nucleophilic reagents including ammonia, aqueous sodium cyanide, and the enamine of cyclohexanone to give the products indicated. Yields obtained by this more cumbersome procedure were inferior to those obtained by the methods described above.
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(12) It is appropriate to note that the results reported here, primarily with **2**, should be compared with an earlier report of Hahn; see ref 3b, in which a one-flask synthesis of 4-chloro-1,2-dimethylbenzene from crude 3,4-dimethyl-4-nitrocyclohexadienyl acetate is described.

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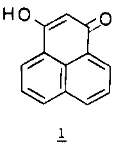
Protonation of Aromatic π Carbocations in Strong Acid. Direct Observation of Protonated Carbocations by ^{1}H NMR Spectroscopy

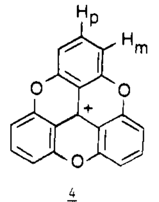
Sir:

Recently we reported evidence for a new type of electrophilic aromatic substitution which involves the reaction of H^+ and D^+ with aromatic π carbocations in strong acid media.[1,2] Although our data clearly indicated that the carbocations were being protonated directly, other mechanisms, although unlikely, could not be completely ruled out. We report at this time observations that constitute proof that the original mechanism is correct.

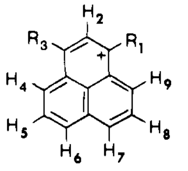
Our original work was done for the most part in triflic acid (CF_3SO_3H and CF_3SO_3D) where the reaction mechanism could be deduced only by inference.[1] Direct observation by ^{1}H NMR spectroscopy of a protonated carbocation, particularly if it were in equilibrium with the original carbocation, e.g., **2a** + $H^+ \rightleftharpoons$ **3a**, would provide overwhelming evidence that carbocations can undergo electrophilic aromatic substitution with positively charged electrophiles. In hopes of accomplishing this, the much stronger acids 1:1 FSO_3H/SbF_5 (magic acid) in SO_2 and SO_2ClF were used.



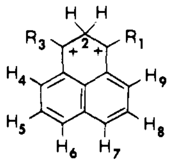
1



4



2



3

a) $R_1 = R_3 = OH$
b) $R_1 = OH,\ R_3 = OEt$
c) $R_1 = R_3 = OEt$
d) $R_1 = OH,\ R_3 = H$
e) $R_1 = R_3 = H$

The bottom ^{1}H NMR spectrum of Figure 1 is that of 3-hydroxyphenalenone (**1**) dissolved in magic acid/SO_2 at −60 °C. This spectrum,[3] which consists of δ 4.94 (br s, 2 H, H-2), 7.90 (t, $J = 8$ Hz, 2 H, H-5 and H-8), 8.83 (d, $J = 8$ Hz, 2 H, H-6 and H-7 or H-4 and H-9), and 8.97 (d, $J = 8$ Hz, 2 H, H-4 and H-9 or H-6 and H-7), is in complete agreement with that expected for the protonated carbocation **3a**. Barely perceptible in the NMR spectrum at −60 °C are peaks at δ 6.25 (s, 1 H, H-2), 7.47 (t, $J = 8$ Hz, 2 H, H-5 and H-8), 8.14 (d, $J = 8$ Hz, H-6 and H-7 or H-4 and H-9), and 8.42 (d, $J = 8$ Hz, 2 H, H-4 and H-9 or H-6 and H-7) which belong to the known monocation **2a**.[1] As seen in the top ^{1}H NMR spectrum of Figure 1, when this sample is warmed to −20 °C, there is a buildup in the monocation (**2a**) concentration and both monocation **2a**

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