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Transfer Hydrogenolysis of Aryl Halides and Other Hydrogen Acceptors by Formate Salts in the Presence of Pd/C Catalyst

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The Pd/C-catalyzed transfer hydrogenolysis of aryl halides by formate salts in a triphase system requires the absorption of all three substrates, the aryl halide acceptor, the formate anion, and the water, to a single site on the catalyst surface in a specific order. This unique mechanism necessitates delicate optimization of reaction conditions. The affinity of various hydrogen acceptors to the catalyst was determined by competitive kinetic experiments to be in the decreasing order: iodobenzene > phenylacetylene > styrene > bromobenzene > nitrobenzene > chlorobenzene > fluorobenzene. The rate-determining step in the overall transfer-hydrogenation process is the adsorption of the donors to the catalyst.

Introduction

One of the most useful applications of catalytic transfer hydrogenation[1-3] is the dehydrohalogenation of aryl halides to yield the corresponding arenes (eq 1) where DH_2 is a

$$DH_2 + ArX \rightarrow D + ArH + HX \qquad (1)$$

hydrogen donor and X is a halide. Typical donors reported in the literature for this application are formic acid[4] and its salts[5-9] as well as several alcohols.[10] Pd/C is the most popular and apparently the most active catalyst in reaction 1, but there are studies using different supports as well as homogeneous palladium catalysts.[8,11] In the presence of formate donors the stoichiometry of the overall reaction is as follows (eq 2):

$$ArX + HCO_2^- \rightarrow ArH + X^- + CO_2 \qquad (2)$$

The simplicity and rapidity of these processes render them as the most attractive alternative for the elimination of halogenated environmental contaminants, e.g., polychlorinated biphenyls (PCB's), phenols, and phenyl ethers.[6]

We proposed potassium and sodium formates as the preferred hydrogen donors for reduction of nitroarenes to areneamines.[12] This recommendation was based on the fact that these salts are *true* hydrogen transfer agents (as no hydrogen gas is released in the course of the reactions, thus stoichiometric amounts of donor and acceptor could be used and no special safety precautions are necessary even in large-scale applications). Hydrogen evolution is, in fact, the main limitation associated with the utilization of ammonium formate as a donor.[7] In addition, potassium and sodium formates were shown to be *recyclable* hydrogen donors.[13] The product, bicarbonate, can be recycled to formate via mild catalytic hydrogenation.[14] It was also demonstrated that although the reaction is very sensitive to the concentration of the water present in the system, this could be optimized to produce high reaction rates even in solid/solid/liquid or solid/liquid/liquid triphase systems.[12] The various homogeneous palladium complexes[8] and the different phase-transfer techniques previously applied[15-17] were evidently not required in the catalytic reaction 2. Actually, in the presence of various surface active ammonium salts or cyclodextrines the reaction takes an additional parallel path to produce biphenyls via reductive dimerization[15,17] (eq 3).

$$2ArX + 2HCOO^- \rightarrow Ar\text{–}Ar + 2X^- + 2CO_2 \qquad (3)$$

Table I. Effect of Solvent on the Hydrogenolysis of Chlorobenzene[a]

solvent	conversion[b]	solvent	conversion[b]
methanol	5	1-butanol	79
ethanol	100	toluene	25
2-propanol	93		

In this article, we present some kinetic observations that shed light on the mechanism of reaction 2, thus assisting in optimization of the process and in understanding its scope and limitations.

Results and Discussion

The catalytic decomposition of aqueous potassium formate to hydrogen and potassium bicarbonate in the presence of Pd/C[18] is completely suppressed when chlorobenzene or bromobenzene is added to the system. The much faster hydrogenolysis reaction 2 is taking place instead. As no reaction could be observed at all in the absence of water it can be concluded that the actual stoichiometry of the overall process is the following (eqs 4–6):

$$ArX + HCO_2^- + H_2O \rightarrow ArH + HCO_3^- + HX \qquad (4)$$

$$HX + HCO_3^- \rightarrow X^- + CO_2 + H_2O \qquad (5)$$

$$\text{net: } ArX + HCO_2^- \rightarrow ArH + X^- + CO_2 \qquad (6)$$

Figure 1 presents a typical reaction profiles for hydrogenolysis of chlorobenzene by potassium formate at 50 °C in the presence of two different initial amounts of water.

Similarly to the reduction of nitroarenes under these conditions[12] this reaction is very sensitive to the amount of water present. This is shown in Figure 2, where the

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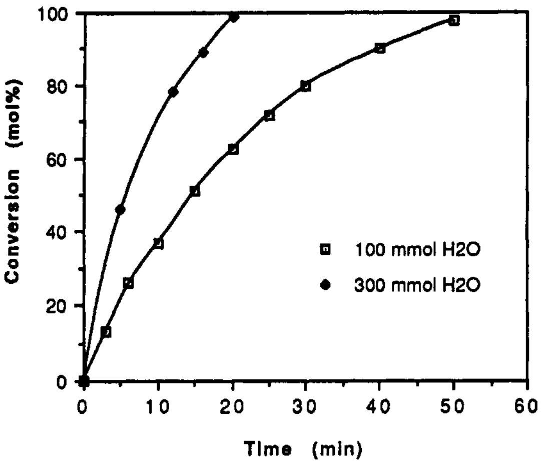

Figure 1. Hydrogenolysis of chlorobenzene by aqueous potassium formate. Experimental conditions: 50 mmol of chlorobenzene in 25 mL of ethanol, 50 mmol of potassium formate in water, 0.2 g of 10% Pd/C, 50 °C.

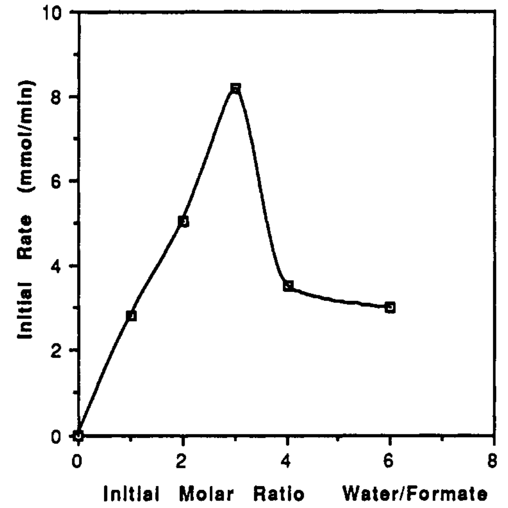

Figure 2. Effect of water on the hydrogenolysis of chlorobenzene. Experimental conditions: as in Figure 1.

initial rate of reaction 2 is plotted vs the initial water/formate molar ratio.

Maximum rate is obtained when the water/formate molar ratio is 3. This effect of water was attributed to the fact that water is an actual reactant in the hydrogen-transfer process and it has to compete with the other two substrates for an adsorption site on the catalyst surface. If the relative ratio of the substrates, including water, is not optimized, lower reaction rates are obtained. When the formate salt is substituted by formic acid no reduction could be detected. The activity could be resumed by in situ neutralization of the acid with potassium or sodium hydroxide. This observation contradicts the procedure reported by Paney and Purkayashta[4] where formic acid was applied directly. We believe that in their system dimethylformamide, which was used as a solvent, reacted with the formic acid to yield small, but sufficient, amounts of ammonium formate.

The effect of several solvents on reaction 5 is summarized in Table I. Alcohols are clearly more effective than toluene with the exception of methanol in which hardly any reaction proved to occur.

It could be observed that methanol was the only solvent in the list to form a single-liquid phase in the reaction mixture while with the other solvents a two-liquid system was obtained. This apparently interfered with the sensitive hydrophilic–lypophilic balance on the catalyst surface avoiding access to one of the substrates (probably water).[12] Ethanol and propanol were recommended as the solvents of choice also by Spatola and co-workers in their study on dehydrohalogenations by ammonium formate.[7] These authors also found an enormous difference in activity between Pd/C catalyst and palladium supported on other carriers (e.g., alumina, silica gel, calcium carbonate, and barium sulfate). We also determined that Pd/C is, by far, the most active catalyst for reaction 2. These unusual variations in activity for different supports can be attributed as well to the critical role of water in the system and to the different wetting properties of the various supports.

Table II. Hydrogenolysis of Haloarenes by Potassium Formate[a]

exp[a]	substrate	time (h)	products (yield %)
1	C_6H_5Cl	1	C_6H_6 (96)
2	4-$CH_3C_6H_4Cl$	1.5	$C_6H_5CH_3$ (87)
3	3-$CH_3C_4H_6Cl$	1	$C_6H_5CH_3$ (92)
4	1,4-$C_6H_4Cl_2$	0.5	C_6H_5Cl (34), C_6H_6 (20)
5	4-BrC_6H_6Cl	1	C_6H_5Br (3), C_6H_5Cl (86)
6	4-$NH_2C_6H_4Cl$	1	$C_6H_5NH_2$ (93)
7	C_6H_5Br	1	C_6H_6 (67)
8	4-$CH_3C_6H_4Br$	1	$C_6H_5CH_3$ (83)
9	2-$CH_3OC_6H_4Br$	1	$C_6H_5OCH_3$ (91)
10	C_6H_5I	3	C_6H_6 (3)
11	C_6H_5F	5	no reaction

[a] Experimental conditions: 50 mmol substrate dissolved in 25 mL of ethanol mixed with 50 mmol of potassium formate in 150 mmol of water, and 0.3 g of 10% Pd/C at 60 °C.

The reduction of both chlorobenzene and bromobenzene by the potassium formate/water system exhibited no kinetic isotope effect when the donors were replaced by either $DCOO^-$ or D_2O or a mixture of both. This behavior is similar to what we found in the reduction of nitroarenes in the same system[12] but is diametrically opposed to what we measured in the catalytic *decomposition* of formate in the absence of a hydrogen acceptor.[18] This observation suggests that the scission of the formate C–H bond or the water O–H bond is not rate determining in the overall reaction.

Several aryl halides were then reduced by potassium formate under similar conditions. Some representative results are summarized in Table II.

Table II indicates that (a) ring substituents have only a minor effect on the hydrogenolysis rate; (b) both aryl chlorides and aryl bromides are effectively reduced by the system; (c) in spite of b, 4-bromochlorobenzene converted to chlorobenzene with high selectivity; (d) fluorobenzene is unaffected under our reaction conditions (note, however, that decomposition of the donors to hydrogen gas takes place in presence of this substrate); and (e) iodobenzene reacts only very slowly. No hydrogen formation was observed in this experiment. It should be noted that, with the exception of fluorobenzene, each of these hydrogenolysis experiments' reactions does eventually reach complete conversion after a certain period of time. The hydrogenolysis rates of chlorobenzene, bromobenzene, and iodobenzene were compared with those of the reduction of other acceptors such as nitrobenzene, styrene, phenylacetylene, benzaldehyde, and benzonitrile. These substrates were (separately) reacted with potassium formate under identical conditions. Kinetic profiles of four of these runs are plotted in Figure 3. Under these conditions benzaldehyde, benzonitrile, and fluorobenzene did not react at all and iodobenzene and phenylacetylene reacted very slowly (conversion was only 2% after 20 min).

These results combined with the fact that substrates that do react suppress any hydrogen formation by direct formate decomposition clearly suggest that the adsorption

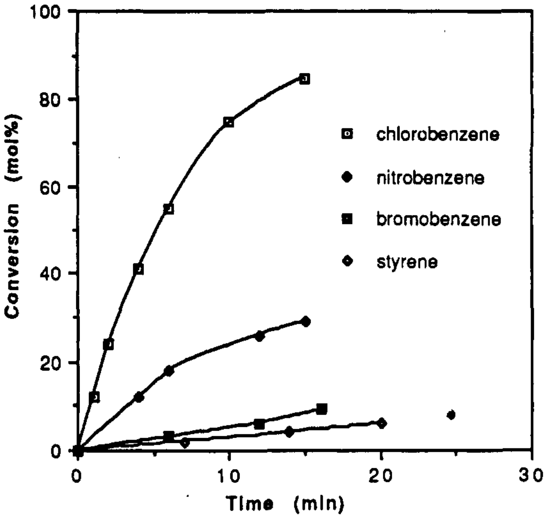

Figure 3. Reaction profiles of transfer hydrogenations of various substrates. Experimental conditions: 50 mmol of substrate dissolved in 25 mL of ethanol, an equivalent amount of potassium formate in 3 equiv of water, 0.2 g of 10% Pd/C, 50 °C.

and activation of the substrate in the hydrogenolysis process is either the rate-determining step or is one of the steps proceeding it.

Particularly interesting observations were made when competitive reduction reactions were performed using mixture of substrates in the same reaction mixture. Results of some of these runs are given in Table III.

The results summarized in Table II along with the findings reported for transfer hydrogenations of nitroarenes by formate salts[12] led to the following conclusions:

(a) On the basis of the fact that the very presence of an acceptor results in the total stop of hydrogen formation via parallel decomposition reaction of the donors indicates that the chemisorption of the acceptor is the initial step of the overall process. This observation also suggests that the free substrates are adsorbed and activated on a single catalytic site.

(b) Among the substrates that *do not* react in the hydrogen-transfer reaction we can distinguish between acceptors that are inactive due to weak adsorption to the catalyst (e.g., fluorobenzene, benzaldehyde) and acceptors that bind too strongly to the catalyst rendering it inaccessible to the donor molecules (e.g., iodobenzene, benzonitrile). Acceptors of the latter group will interfere with the reduction of other substrates as well as with hydrogen formation via formate decomposition. The presence of substrates from the first group, however, will not affect any of these reactions.

(c) The adsorption of the acceptor to the catalytic surface is obviously not the rate-determining step in the overall process. Otherwise, substrates with high adsorption constants would have been reduced faster and vice versa. This is in agreement with our studies on transfer hydrogenation of nitroarenes where it was shown that the adsorption of the aqueous donors is the slow step in the process.

(d) In view of the effect that the various acceptors have on the reduction of their counterparts we can estimate that the adsorption constant is decreasing in magnitude according to the following descending order: benzonitrile > iodobenzene > phenylacetylene > styrene > bromobenzene > nitrobenzene > chlorobenzene > benzaldehyde > fluorobenzene.

On the basis of these observations we propose the following single-site four-step mechanism for the hydrogenolysis reactions of aryl halides, which is similar to the

Table III. Competetive Transfer Hydrogenation with Potassium Formate[a]

exp[a]	reactants	products (mol %)
1	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3$ + $4\text{-ClC}_6\text{H}_4\text{CH}_3$	$4\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3$ (52) + $\text{C}_6\text{H}_5\text{CH}_3$ (12) + $4\text{-ClC}_6\text{H}_4\text{CH}_3$ (35)
2	$4\text{-BrC}_6\text{H}_4\text{CH}_3$ + $4\text{-ClC}_6\text{H}_4\text{CH}_3$	$\text{C}_6\text{H}_5\text{CH}_3$ (51) + $4\text{-ClC}_6\text{H}_4\text{CH}_3$ (49)
3	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3$ + $4\text{-BrC}_6\text{H}_4\text{CH}_3$	$4\text{-NH}_2\text{C}_6\text{H}_4\text{CH}_3$ (>1) + $4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3$ (51) + $\text{C}_6\text{H}_5\text{CH}_3$ (10) + $4\text{-BrC}_6\text{H}_4\text{CH}_3$ (38)
4	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3$ + $4\text{-C}_6\text{H}_5\text{CH}{=}\text{CH}_2$	$4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_3$ (50) + $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ (7) + $\text{C}_6\text{H}_5\text{CH}{=}\text{CH}_2$ (40) + $4\text{-NH}_2\text{C}_6\text{H}_5\text{CH}_3$ (>2)
5	$4\text{-ClC}_6\text{H}_4\text{CH}_3$ + $\text{C}_6\text{H}_5\text{CH}{=}\text{CH}_2$	$4\text{HClC}_6\text{H}_4\text{CH}_3$ (50) + $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ (10) + $\text{C}_6\text{H}_5\text{CH}{=}\text{CH}_2$ (39)
6	$4\text{-IC}_6\text{H}_4\text{NO}_2$	$4\text{-IC}_6\text{H}_4\text{NO}_2$ (97) + $\text{C}_6\text{H}_5\text{NO}_2$ (3)
7	$\text{C}_6\text{H}_5\text{NO}_2$ + $\text{C}_6\text{H}_5\text{I}$	$\text{C}_6\text{H}_5\text{NO}_2$ (49) + C_6H_6 (2) + $\text{C}_6\text{H}_5\text{I}$ (49)
8	$4\text{-FC}_6\text{H}_4\text{NO}_2$	$4\text{-FC}_6\text{H}_4\text{NH}_2$ (100)
9	$\text{C}_6\text{H}_5\text{NO}_2$ + $\text{C}_6\text{H}_5\text{F}$	$\text{C}_6\text{H}_5\text{NH}_2$ (51) + $\text{C}_6\text{H}_5\text{F}$ (50)
10	$\text{C}_6\text{H}_5\text{NO}_2$ + $\text{C}_6\text{H}_5\text{CHO}$	$\text{C}_6\text{H}_5\text{NH}_2$ (48) + $\text{C}_6\text{H}_5\text{CHO}$ (50)

[a] Experimental conditions: 25 mmol of each substrate dissolved in 50 mL of ethanol, 100 mmol of potassium formate in 300 mmol of water, and 0.3 g of 10% Pd/C mixed at 70 °C for 15 min.

mechanism proposed for the transfer hydrogenation of nitroarenes:

(1) Chemisorption of the halogenated acceptor ArX to catalyst active site C.

$$\text{ArX} + \text{C} \rightleftharpoons \text{C(SX)}$$

(2) Chemisorption of the aqueous-phase donors (formate anion F and water W).

$$\text{C(ArX)} + \text{F} + \text{W} \rightleftharpoons \text{C(ArX)FW}$$

(3) Hydrogen transfer on the catalyst surface with formation of dehalogenated product ArH, bicarbonate anion B, and hydrogen halide HX.

$$\text{C(ArX)FW} \rightarrow \text{C(ArH)B(HX)}$$

(4) Desorption of the product and regeneration of the catalyst C for a new catalytic cycle.

$$\text{C(ArH)B(HX)} \rightarrow \text{C} + \text{ArH} + \text{X}^- + \text{CO}_2$$

No parallel direct adsorption of formate or water molecule to a free catalytic site is possible. On the other hand, with the more active substrates (iodobenzene, benzonitrile), saturation of the catalytic sites by adsorption of more than one acceptor molecule per site is apparently possible resulting in inhibition of the reduction process:

$$\text{C(ArX)} + \text{SX} \rightleftharpoons \text{C(ArX)}_2$$

Due to the absence of a kinetic isotope effect in experiments where deuterated donors were applied, we believe that step 3 is not the rate-determining step in the reaction, which is evidently one of the preceding steps. The adsorption of the substrate (step 1) is relatively a fast process and although it affects the observed rate is definitely not rate determining. This leaves us with the conclusion that the adsorption of the donors, step 2 (or one of the donors), is the slow step and rate determining in the hydrogen-transfer reaction.

Experimental Section

Materials and methods used in this study were reported earlier.[12]

Reduction of 4-Chlorotoluene. To a 100-mL three-necked round-bottom flask equipped with a mechanical stirrer, reflux condenser, and a thermometer which was placed in a thermostatic bath were introduced the following: 4.20 g (50 mmol) of potassium formate, 2.61 g of water (145 mmol), 6.35 g (50 mmol) of 4-

chlorotoluene, and 50 mL of ethanol. The mixture was stirred and heated to 50 °C, 0.2 g of 10% Pd/C catalyst (50% water, 0.09 mmol Pd) was added, and the heterogeneous system was mixed for 1 h at the above temperature. After being cooled, the aqueous phase was separated, the solvent evaporated under vacuum, and the crude product washed with water and distilled. Pure toluene (4.18 g; 91%) was obtained.

Registry No. PhCl, 108-90-7; *p*-MeC$_6$H$_4$Cl, 106-43-4; *m*-MeC$_6$H$_4$Cl, 108-41-8; *p*-ClC$_6$H$_4$Cl, 106-46-7; *p*-BrC$_6$H$_4$Cl, 106-39-8; *p*-H$_2$NC$_6$H$_4$Cl, 106-47-8; PhBr, 108-86-1; *p*-MeC$_6$H$_4$Br, 106-38-7; *o*-MeC$_6$H$_4$Br, 578-57-4; PhI, 591-50-4; PhF, 462-06-6; *p*-IC$_6$H$_4$NO$_2$, 636-98-6; *p*-O$_2$NC$_6$H$_4$Me, 99-99-0; PhCH=CH$_2$, 100-42-5; *p*-FC$_6$H$_4$NO$_2$, 350-46-9; PhNO$_2$, 98-95-3; PhC≡CH, 536-74-3; HCO$_2$H·K, 590-29-4; Pd, 7440-05-3.

Oxyfunctionalization of Hydrocarbons. 17.[1] Acid-Dependent High Regioselectivity Hydroxylation of Naphthalene with Hydrogen Peroxide Giving 1- or 2-Naphthol

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The acid-catalyzed hydroxylation of naphthalene with 90% hydrogen peroxide was investigated. Regioselectivity of the reaction depends on the acidity of the system and the solvent used. In anhydrous hydrogen fluoride or 70% HF–30% pyridine solution at −10 to +20 °C 1-naphthol is the product formed in >98% selectivity. In contrast, 2-naphthol is obtained in hydroxylation in superacid (HF–BF$_3$, HF–SbF$_5$, HF–TaF$_5$, FSO$_3$H–SbF$_5$) solution at −60 to −78 °C in >98% selectivity. When 1-naphthol reacted under the latter conditions 1,5- and 1,7-dihydroxynaphthalene were obtained, while 2-naphthol gave 1,6-dihydroxynaphthalene (along with only minor amounts of 1,7-dihydroxynaphthalene). The mechanism of the reactions is discussed, contrasting electrophilic hydroxylation of naphthalene, giving predominantly 1-substitution, with reaction of protonated naphthalenes (i.e., naphthalenium ions) with hydrogen peroxide.

Introduction

Studies of electrophilic aromatic oxygenation using various peroxide reagents have been reported. These include hydrogen peroxide in the presence of sulfuric acid[2] or boron trifluoride etherate,[3] peracids,[4] peracids with Lewis acid promoters,[5] diisopropyl peroxydicarbonate,[6] aroyl peroxides,[7] dicyclohexyl peroxydicarbonate–ferric chloride,[8] alkyl peroxides,[9] and dialkyl peroxides.[10] More recently, effective electrophilic hydroxylation of aromatics was carried out using hydrogen peroxide and hydrogen fluoride,[11] aluminum chloride[12] or superacid catalysts.[13] Application of hydrogen peroxide with pyridinium polyhydrogen fluoride was also described.[14]

Few reports appeared in the literature on the direct hydroxylation of naphthalene. Williams et al. have reported the reaction of aroyl peroxides with naphthalene via homolytic substitution.[15] Friedel–Crafts oxygenation of naphthalene with diisopropyl peroxydicarbonate gives a low yield of naphthols. Vesely and Schmering reported hydroxylation with hydrogen peroxide–hydrogen fluoride under carbon dioxide pressure.[11]

In our continued study of electrophilic oxyfunctionalization of hydrocarbons, we report now the investigation of the acid-catalyzed hydroxylation of naphthalene with 90% hydrogen peroxide and the surprising observation of extremely high regioselectivity in obtaining either 1- or 2-naphthol, dependent on the acidity of the catalyst systems and the solvent used.[16]

Results and Discussion

Naphthalene was treated with 90% hydrogen peroxide at temperatures between −78 and 0 °C in solutions of various acids and superacids such as fluorosulfuric acid–sulfuryl chloride fluoride, fluorosulfuric acid–sulfur dioxide, fluorosulfuric acid, fluorosulfuric acid–methylene chloride, fluorosulfuric acid–antimony pentafluoride (1:1) sulfuryl chloride fluoride, hydrogen fluoride, hydrogen fluoride–sulfuryl chloride fluoride, 70% hydrogen fluoride–30% pyridine, hydrogen fluoride–boron trifluoride, hydrogen fluoride–tantalum pentafluoride, hydrogen fluoride–antimony pentafluoride, and trifluoromethanesulfonic acid–sulfuryl chloride fluoride. 1- and 2-naphthol were obtained, together with some dihydroxynaphthalenes and poly-

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