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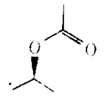
(19) For a leading reference see J. K. Kochi and J. W. Powers, *J. Am. Chem. Soc.*, **92**, 137 (1970). The 2,3-sigmatropic shift of a Cr^{VI} alkyl such as **3** would be expected to be very fast.

(20) Persuasive arguments that the oxidation of allylic alcohols proceeds via Cr^{VI}-olefin π complex → Cr^{VI}–C σ complex have been made: P. Sundararaman and W. Herz, *J. Org. Chem.*, **42**, 813 (1977). These workers also argue against the involvement of charged species such as **5** in Scheme II. However, since the question is still not resolved, Scheme II is included here for completeness.

(21) Oxidation of olefins with CrO_2Cl_2 has also been argued to proceed via the initial formation of a CrO_2Cl_2 olefin π complex, followed by rearrangement to a σ complex: K. B. Sharpless, A. Y. Teranishi, and J-E. Bäckvall, *J. Am. Chem. Soc.*, **99**, 3120 (1977).

(22) The formation of such a radical cation could rationalize the abundant formation of 5β,6β-epoxide with those reagents such as $Na_2CrO_4/AcOH/Ac_2O$ which are accompanied by nucleophilic species. Axial attack[18] by acetate at the 6β position of the radical cation **5** leads to the radical **13**, further



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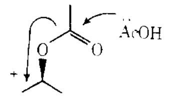

14

oxidized by electron transfer to the tertiary carbonium ion **14**, which cyclizes to the oxide with the formation of acetic anhydride. In aqueous systems, of course, water would be the nucleophile.

(23) As in Scheme I the formal proton transfer from N to O designated in **6** → **7** could occur after this second electron transfer.

(24) See, for example, G. Dyrkacz and J. Rocek, *J. Am. Chem. Soc.*, **95**, 4756 (1973); E. J. Corey and L. S. Melvin, *Tetrahedron Lett.*, 929 (1975).

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(26) It has been clearly established that other eneophiles such as singlet oxygen[27] and diazodimethyl dicarboxylate[28] attack Δ^5-, Δ^6-, and $\Delta^{5,7}$-steroids exclusively from the α face. It is curious that the Sharpless[29] mechanism for allylic oxidation with SeO_2 requires that the initial ene reaction take place from the β side since the SeO_2 oxidation of Δ^5-steroids gives mixtures of 4β-hydroxy-Δ^5-, and 6β-hydroxy-Δ^4-steroids.[30] (Only the former is explicable by the Sharpless mechanism.) Work is in progress in our laboratory toward explaining this dichotomy.

(27) See, for example. G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957); A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **83**, 1498 (1961).

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(30) For example, see O. Rosenheim and W. W. Starling, *J. Chem. Soc.*, 377 (1937); A. Butenandt and E. Hausmann, *Ber. Dtsch. Chem. Ges.*, **70**, 1154 (1937); and C. A. Kind and W. Bergmann, *J. Org. Chem.*, **7**, 341 (1942).

(31) For other examples, see W. G. Salmond, U.S. Patent 4 006 172 (February 1, 1977).

Electrocatalytic Hydrogenation of Aromatic Compounds

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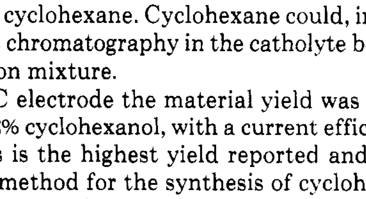
We are currently interested in exploring electrocatalytic organic reactions and report here some initial results which survey electrohydrogenations of aromatic compounds. This particular aspect of electrocatalysis seems to have obtained only limited attention. The possibility of hydrogenation at the very mild conditions normally employed in electrosynthesis, room temperature, and atmospheric pressure is, however, attractive. Furthermore, the electrochemical production of hydrogen directly at the surface of the catalyst would circumvent the compression, transportation, and storage of hydrogen.

Electrocatalytic hydrogenation of olefins has been the subject of numerous investigations employing both precious metal catalyst electrodes,[1-3] like palladium, platinum, and rhodium, as well as "spongy" nickel. The latter is capable of hydrogenating activated double and triple bonds in very good yields.[4,5]

The reduction of aromatic compounds was discovered long ago. Early workers[6,7] hydrogenated phenol in dilute H_2SO_4 at a platinized platinum (Pt|Pt) cathode to cyclohexanol in fair material yield, but with low current efficiency. Under similar conditions[8] the three isomeric cresols have been hydrogenated, yielding in each case an unseparated mixture of alcohols and ketone. The electrocatalytic hydrogenations of cinnamic acid, phenylacetic acid, and benzoic acid at a Pt|Pt cathode in a pressurized cell have also been reported.[9]

The most widely used electrode in electrocatalytic hydrogenation has been a platinum electrode covered with different kinds of metal "blacks".[2,3] To reduce cost we investigated the use of carbon rods as the conductive base for the catalyst, an approach recently successfully applied in other fields of electrocatalysis.[10] These electrodes were used to hydrogenate several aromatic compounds. As shown in Tables I and II we were able to hydrogenate different phenols, anisole, aniline, benzoic acid, cumene, and *tert*-butylbenzene to the corresponding cyclohexyl compounds in fair to excellent yields. Special attention was given to phenol reduction, in part because we wished to evaluate the competition between hydrogenation and hydrogenolysis of the hydroxy group. The hydrogenation of phenol in dilute H_2SO_4 was initially shown to be much more efficient on a Pt|C electrode than on Pt|Pt. After passage of the theoretical amount of electricity (6 F/mol) at a Pt|C electrode, the isolated mixture contains cyclohexanone (**2**, R = H) and cyclohexanol (**3**, R = H) together with phenol (**1**, R = H).



1 2 3

If a larger amount (12 F/mol) of current is passed the only isolated product is cyclohexanol. The material yield though is still low, suggesting a high degree of hydrogenolysis to benzene and cyclohexane. Cyclohexane could, indeed, be detected by gas chromatography in the catholyte before workup of the reaction mixture.

On a Rh|C electrode the material yield was much higher producing 92% cyclohexanol, with a current efficiency as high as 79%. This is the highest yield reported and it is a quite satisfactory method for the synthesis of cyclohexanols. The observed difference between platinum and rhodium is very similar to the results obtained in normal catalytic hydrogenation where platinum is known to give considerable hydrogenolysis of phenols and phenyl ethers as compared to a rhodium catalyst.[11,12]

It is also clear from the results in Table I that the activity of the catalyst metals follows at least qualitatively the se-

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Table I. Electrocatalytic Hydrogenation of Phenols[a]

					Yield, %				
1, R =	Registry no.	Cathode	*i*, A	*F*, mol	2	Registry no.	3	Registry no.	1
H	108-95-2	Pt/Pt	0.1	6	7	108-94-1	17	108-93-0	50
H		Pt/C	0.8	6	6		43		11
H		Pt/C	0.8	12			54		
H		Rh/C	0.2	6	8		77		
H		Rh/C	0.8	6	15		74		1
H		Rh/C	0.8	7.2			92		
H		Pd/C	0.2	6	6		2		74
H		Pd/C[b]	0.2	6	15		5		49
2-Methyl	95-48-7	Rh/C	0.2	6	29	583-60-8	45[c]		12
2-Methyl		Rh/C	0.8	6	24		43[d]		9
2-Methyl		Rh/C	1.0	6	30		42[e]		14
2-Methyl		Rh/C	0.8	10.8			83[f]		
2,6-Dimethyl	576-26-1	Rh/C	0.8	6	28	2816-57-1	39	5337-72-4	20
2,6-Dimethyl		Rh/C	0.8	12	1		82		
2,3-Dimethyl[g]	526-75-0	Rh/C	0.8	6	10	13395-76-1	17	1502-24-5	63
2,3-Dimethyl[g]		Rh/C	0.8	12	7		73		9
5,6,7,8-Tetrahydro-1-naphthol[h]	1125-78-6	Rh/C	0.2	20.4	20	4832-17-1	46	825-51-4	6
2-Naphthol[h]	135-19-3	Rh/C	0.2	21	44[i]				5

[a] 0.2 M H_2SO_4 as catholyte. [b] Catholyte heated to 65 °C. [c] 80 cis:20 trans. [d] 83 cis:17 trans. [e] 87 cis:17 trans. [f] 70 cis:30 trans. [g] Catholyte heated to 40 °C. [h] Catholyte heated to 65 °C. [i] 5,6,7,8-Tetrahydro-2-naphthol.

Table II. Electrocatalytic Hydrogenation of Aromatic Compounds[a]

Reactant			Yields, %	
C_6H_5–X, X =	*i*, A	*F*, mol	$C_6H_{11}X$	C_6H_5X
NH_2	0.8	12	73	
CO_2H	0.2	10	63	31
$(CH_3)_2CH$	0.2	8.4	56	23
$(CH_3)_3C$	0.2	10	33	51
OCH_3	0.8	6	54[b]	5
OCH_3	0.8	12	50[c]	
1-Methylnaphthalene	0.4	9		95

[a] Using Rh|C in 0.2 M H_2SO_4. [b] Also cyclohexanone (14), cyclohexanol (1). [c] Also cyclohexanol (25).

quence established from "normal" catalytic hydrogenation.[11] Only platinum and rhodium, which are known to hydrogenate aromatic nuclei at atmospheric pressure,[12,13] are effective under the applied electrochemical conditions. Palladium, which requires increased pressure and temperature for normal hydrogenation, gives only low electrocatalytic conversion, and nickel, which normally requires very severe conditions,[11] gives no electrohydrogenation at all; instead hydrogen is evolved and phenol is recovered.

Table I also shows, with hydrogenation of *o*-cresol (**1**, R = 2-methyl) as an example, that variation of the current density from 0.2–1.0 Å (approximate geometric area of the electrode, 68 cm^2) only has a small effect on the current efficiency. Therefore, hydrogenations could be performed at a high current density to reduce the time scale of the experiment. It is also clear that the current efficiency is a function of the concentration of substrate as shown by the total depression of the hydrogen evolution in the beginning of the experiment but not at the end.

The electrocatalytic hydrogenation of *o*-cresol produced 2-methylcyclohexanol stereoselectively with a cis:trans ratio of 70:30. This is in accordance with results obtained from catalytic hydrogenation of *o*-cresol on a Rh catalyst.[14] As reported we also found that the hydrogenation of 2-methylcyclohexanone gave approximately a 50:50 mixture of the cis and trans alcohols, therefore, the hydrogenation of *o*-cresol cannot all take place through the ketone, and indeed the cis:trans ratio of the alcohol was higher when the hydrogenation was stopped before the total conversion of the ketone to the alcohol. The hydrogenation of 2,6-dimethylphenol also produced one isomer with very high selectivity (82%). From NMR the structure of this isomer was shown to be *cis,cis*-2,6-dimethylcyclohexanol.

Both β-naphthol and 5,6,7,8-tetrahydro-1-naphthol are rather insoluble in water and hydrogenation is not successful on Rh|C at room temperature. We were, however, able to hydrogenate these compounds by heating the catholyte, which allowed sufficient material to dissolve. β-Naphthol gave almost exclusively 5,6,7,8-tetrahydro-2-naphthol which was not further hydrogenated. 5,6,7,8-Tetrahydro-1-naphthol, on the other hand, was hydrogenated (on a fresh catalyst electrode) to a mixture of the decalones and decalols. The current yield, however, was low in both cases and the electrode was somewhat poisoned after each hydrogenation, which probably explains why the hydrogenation of β-naphthol stopped at the tetrahydro stage.

Solvent effects were investigated and a pronounced decrease in catalyst activity due to organic solvents was found. The addition of just 5% methanol to the aqueous catholyte decreases the activity of the Rh|C catalyst electrode toward hydrogenation of phenol. Recovery of 68% **1**, 27% **2**, and only 5% cyclohexanol **3** was observed when 15% methanol in 0.2 M H_2SO_4 was used and 6 F/mol were passed. The same effect was found by addition of ethanol, butanol, dioxane, and acetic acid. The size of the inhibiting effect is dependent on the activity of the particular electrode. Thus, freshly prepared Rh|C electrodes were less sensitive to this cosolvent effect than similar electrodes which had been previously used.

The effect of the organic cosolvent is readily visible since hydrogen evolution at a Pt|C or Rh|C cathode in aqueous H_2SO_4 is totally depressed by addition of phenol to the catholyte. If, however, an organic cosolvent is present, little depression of the hydrogen evolution is observed. The effect of the solvent seems to be the exclusion of the phenol from the catalyst by competitive adsorbtion in such a way that the reduction of protons is still possible. This effect must also be present in catalytic hydrogenations. In that case only the rate, not the yield, is affected because the system is closed. The electrochemical system used here is, however, open and hydrogen gas is lost.

This inhibition by organic cosolvents limits the presently constituted method. Although quite insoluble liquid aromatics like cumene and *tert*-butylbenzene were hydrogenated satisfactorily by using rapid stirring of the suspension, α-methylnaphthalene proved to be inert.

Experimental Section

All hydrogenations were performed in a divided H-type cell with two glass frits of medium porosity as the dividing membrane. The catholyte volume was approximately 100 mL. The electrolyte was 0.2 M H_2SO_4, and the working electrode consisted of six carbon rods (6 mm diameter, 100 mm long), onto which the catalyst metal had been electroplated. The geometric area of the catalyst electrode was approximately 69 cm^2. A piece of Pt sheet was used as the counter electrode. This assured that the anodic reaction was the production of O_2. All experiments were performed at constant current using a H.P. 6266B DC power supply.

The plating solutions used for cathode preparation were either a 2% aqueous H_2PtCl_6 solution, a 2% $RhCl_3$ solution in 0.1 M H_2SO_4, or a 2% $PdCl_2$ solution in 0.1 M H_2SO_4. In one case the H_2PtCl_6 supplied by Alfa Ventron failed to give the expected platinum black plating. Each carbon rod was plated separately centered in a cylindrical Pt-sheet anode using 1 A for 5 min. The Ni|C electrodes were plated from a solution of 10 g of $NiSO_4$ in 50 mL of H_2O + 50 mL of concentrated NH_4OH with a current of 1 A for 5 min.

Most hydrogenations were performed using 2 g of substrate. After the electrolysis was stopped the catholyte was extracted either directly or in the case of hydrogenation of aniline, after basification with $NaHCO_3$, with 5 × 100 mL of CH_2Cl_2, dried over $MgSO_4$, and evaporated.

The products were identified by NMR of the reaction mixture and comparison of the gas liquid chromatography (GC) retention times with these of authentic samples, or after isolation by preparative GC or high-pressure liquid chromatography by their NMR and MS data. Quantitation was performed by GC using internal standards. Current yields were calculated using an assumed stoichiometry of 6 e$^-$/molecule.

The most abundant isomer of 2,6-dimethylcyclohexanol, produced in 82%, gave a NMR spectrum with a sharp doublet at 1.0 ppm demonstrating equivalency of the two methyls. The methine proton next to the hydroxyl group gave an unresolved singlet at 3.55 ppm with no observable splitting indicating an axial–equatorial or equatorial–equatorial coupling. On this basis the isomer was identified as the *cis,cis*-2,6-dimethylcyclohexanol.

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Registry No.—*cis*-3 (R = 2-Me), 7443-70-1; *trans*-3 (R = 2-Me), 7443-52-9.

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Chemistry of Sulfenamides. 1. Study of the Rearrangements of Sulfenanilides

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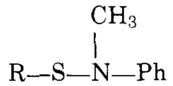
The thermal rearrangement of *N*-arylsulfenamides was first reported by Zincke and Eismayer.[1] Later the rearrangement of various sulfenanilides was studied by Moore and Johnson,[2] and the rearrangement of *N*-thiazolylsulfenamides was reported by Hoggarth.[3] More recently, the rearrangement has been studied by Davis and co-workers.[4] We would like to report here the results of our studies on the rearrangements of *N*-methylalkanesulfenamides Ia–d.



$$R\text{—}S\text{—}\overset{\overset{\displaystyle CH_3}{|}}{N}\text{—}Ph$$

Ia, R = CH_3
b, R = C_2H_5
c, R = *i*-C_3H_7
d, R = *t*-C_4H_9

The sulfenamides were prepared by reaction of the appropriate sulfenylchloride with *N*-methylaniline and purified by vacuum distillation. Unless care was taken the methanesulfenanilide (Ia) rearranged to a mixture of *o*- and *p*-methylthio-*N*-methylanilines during distillation; however, the ethane, 1-methylethane- and 1,1-dimethylethanesulfenanilides could be vacuum distilled without decomposition. The structures of the sulfenanilides were confirmed by examination of their spectra and the observation that under acidic conditions in the presence of iodide ion iodine was liberated.[5,6] The NMR spectra of Ia–Id exhibited resonances for the *N*-methyl groups, the *S*-alkyl groups, and 5-aromatic protons and established that the sulfur atom was attached to the nitrogen atom and not to the aromatic ring.

Upon heating Ia neat at 150 °C in an oil bath, it was observed that it was transformed into a mixture of *o*- and *p*-methylthio-*N*-methylanilines. Vacuum distillation of the crude rearrangement products followed by column chromatography of the sulfide-containing fraction over Florisil in hexane gave 2-methylthio-*N*-methylaniline (IIa) and 4-methylthio-*N*-methylaniline (IIIa) as pure liquids. These compounds were identified by their spectroscopic properties. The NMR spectrum of the ortho isomer showed a complex coupling pattern between δ 7.5 and 6.3 that gave an integrated area of four protons, a broad peak for the amino hydrogen at δ 4.75, a three-proton singlet at δ 2.76 for the *N*-methyl group, and a three-proton singlet at δ 2.18 for the *S*-methyl group. The IR spectrum indicated the presence of the N–H group and an absorption band at 750 cm^{-1} which indicated that this was the ortho isomer. The para isomer gave an NMR spectrum that was composed of an aromatic region, δ 7.48 to 6.15, characteristic of the AA′BB′ system of a para-disubsitituted benzene, a broad N–H singlet at δ 4.68, a three-proton singlet for the *N*-methyl group at δ 2.6, and a three-proton singlet for the *S*-methyl group at δ 2.25. The IR spectrum indicated the presence of the N–H group and an absorption band at 820 cm^{-1} which further substantiated the assignment of the para structure. The same products were obtained upon heating Ia at 60 °C in CCl_4, acetonitrile, or CCl_4 with HBr in acetic acid added.

The ethanesulfenanilide (Ib) rearranged as did Ia upon heating in CCl_4 at 60 °C, and the products were separated and identified by the same general procedure just described, the only difference being the presence of an *S*-ethyl group in place of an *S*-methyl group. Under the same conditions, the rearrangement of the *S*-isopropyl, Ic, and *S*-*tert*-butyl, Id, derivatives was not observed, the only products of these attempted rearrangements being *N*-methylaniline and mixtures of dialkyl di- and trisulfides. Heating Ic neat at 150 °C gave a mixture of *N*-methylaniline, isopropyl sulfide, and isopropyl trisulfide. Refluxing Ic in acetonitrile with a trace of *p*-toluenesulfonic acid added gave *N*-methylaniline and isopropyl disulfide as the only identifiable products and heating Ic in benzene with aluminum chloride gave *N*-methylaniline, isopropyl disulfide, and isopropyl trisulfides. Refluxing Ic in

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