Experimental Section

A Beckman GC-4 chromatographic instrument equipped with a thermal conductivity detector and an 8 ft × 0.25 in. column of 20% diethylene glycol succinate on Chromosorb W, AW-DMCS (45–60 mesh) and a Bausch and Lomb IR 270 spectrophotometer were used for analytical work.

Cyclobutyl *p*-nitrobenzenesulfonate resulted when *p*-nitrobenzenesulfonyl chloride (7.2 g, 35 mmol) was mixed with cyclobutanol (2.16 g, 30 mmol) and 40 ml of dry pyridine at 0°. After standing for 20 hr at 0°, the thick reaction mixture was carefully hydrolyzed by the slow addition of 20 ml of cold water at 0–5° followed by the rapid addition of sufficient cold, dilute HCl to acidify the mixture. The precipitated ester was separated on a Buchner funnel and washed several times with cold, dilute HCl, several times with cold water and then with cold petroleum ether (bp 30–60°) to yield the crude ester. Recrystallization from petroleum ether–benzene gave 5.0 g (65%) of light yellow crystals, mp 64–68°. Two additional recrystallizations yielded the analytical sample, mp 68–69°.

Anal. Calcd for $C_{10}H_{11}NO_5S$: C, 46.69; H, 4.31; N, 5.45. Found: C, 46.63; H, 4.39; N, 5.60.

Cyclobutyl *p*-bromobenzenesulfonate was prepared from *p*-bromobenzenesulfonyl chloride as described above in 63% yield: mp (after two recrystallizations from 33:1 petroleum ether–benzene) 53–54° (lit.[18] mp 52–53.5°).

Cyclobutyl Benzenesulfonate.—To 3.6 g (50 mmol) of cyclobutanol in 50 ml of dry pyridine cooled to 0° was added 9.7 g (55 mmol) of benzenesulfonyl chloride. After standing for 24 hr at 5° and an additional 28 hr at 18°, the mixture was carefully hydrolyzed by the slow addition of 20 ml of cold water at 0–5° followed by the rapid addition of sufficient cold, dilute HCl to acidify the mixture. The separated oil was taken up in 40 ml of methylene chloride, washed twice with cold, dilute HCl and once with cold, saturated $NaHCO_3$, dried over Na_2SO_4, and concentrated to yield an oil. The crude ester was purified twice by stirring with petroleum ether, freezing the undissolved oil at −78°, decanting off the solvent, and removing the last traces of solvent under reduced pressure (*ca.* 0.1 mm) to yield 5.5 g (52%) of an oil. The purity, calculated from infinity titers of the ethanolyses, was 99%. The ir spectrum, ν_{SO_2} (asymmetric) 1360 and ν_{SO_2} (symmetric) 1170 cm^{-1}, was consistent with the assigned structure.

Cyclobutyl *p*-toluenesulfonate was prepared in 50% yield by published procedure:[19] mp 25° (lit.[19] mp 24–25°); ir (neat) 1357 (ν_{SO_2}, asymmetric) and 1173 cm^{-1} (ν_{SO_2} symmetric).

Cyclobutyl *p*-methoxybenzenesulfonate was prepared from *p*-methoxybenzenesulfonyl chloride as described for cyclobutyl benzenesulfonate in 59% yield. The purity of the oil, calculated from infinity titers of the ethanolyses, was 99%. The ir spectrum, ν_{SO_2} (asymmetric) 1358 and ν_{SO_2} (symmetric) 1170 cm^{-1}, was consistent with assigned structure.

Cyclobutyl methanesulfonate was prepared from methanesulfonyl chloride as described for cyclobutyl benzenesulfonate in 40% yield. The purity of the oil, calculated from infinity titers of the ethanolyses, was 99%; ir (neat) 1340 (ν_{SO_2}, asymmetric) and 1170 cm^{-1} (ν_{SO_2}, symmetric).

Solvents.—Absolute ethanol was prepared according to the method of Fieser.[20] Acetic acid solvent was prepared from 994.9 ml of glacial acetic acid (Matheson Scientific, 99.8%) and 5.1 ml of acetic anhydride. 2,2,2-Trifluoroethanol (Aldrich Chemical Co.) was redistilled just prior to use.

Acetolysis Product Studies. A. Cyclobutyl *p*-Bromobenzenesulfonate.—Cyclobutyl *p*-bromobenzenesulfonate (1.5 g, 5 mmol) was dissolved in sufficient acetic acid solvent (containing 7 mmol of urea) to give 25 ml of solution. After 10 half-lives at 50°, the solution was diluted with 150 ml of water and continuously extracted with ether for 24 hr. The ether extract was neutralized with $NaHCO_3$ and dried (Na_2SO_4), and most of the solvent was removed by distillation. Analysis by gc revealed, in addition to solvent, the presence of allylcarbinyl acetate, cyclobutyl acetate, and cyclopropylcarbinyl acetate in the ratio 1.0:10.2:13.7, respectively.

B. Cyclobutyl *p*-Methoxybenzenesulfonate.—Cyclobutyl *p*-methoxybenzenesulfonate (1.2 g, 5 mmol) was solvolyzed in 25 ml of acetic acid solvent (containing 7 mmol of urea) for 10 half-lives at 50°. The material was worked up as before and analysis by gc revealed, in addition to solvent, the presence of allylcarbinyl acetate, cyclobutyl acetate, and cyclopropylcarbinyl acetate in the ratio 1.0:10.5:13.5, respectively.

C. Cyclobutyl Methanesulfonate.—Cyclobutyl methanesulfonate (0.53 g, 5 mmol) was solvolyzed as above for 10 half-lives at 50°. The material was worked up as before and analysis by gc revealed, in addition to solvent, the presence of allylcarbinyl, cyclobutyl, and cyclopropylcarbinyl acetate in the ratio 1.0:10.2:13.7, respectively.

Rate measurements were accomplished by usual ampoule techniques.[21] The titrating solutions were, for ethanolysis and 2,2,2-trifluoroethanolysis, 0.020 *N* sodium methoxide in anhydrous methanol and, for acetolysis, 0.020 *N* sodium acetate in acetic acid. The indicators used were bromthymol blue (in water), bromphenol blue (in 20% aqueous EtOH), and bromphenol blue (in acetic acid), respectively.

Registry No.—EtOH, 64-17-5; AcOH, 64-19-7; CF_3CH_2OH, 75-89-8.

(18) I. Lillien and L. Handloser, *J. Amer. Chem. Soc.*, **93**, 1682 (1971).
(19) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951).
(20) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1957, p 285.
(21) D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964).

The Electrochemical Reduction of Aromatic Acids to the Corresponding Aldehydes

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A number of aromatic carboxylic acids have been found to undergo electrochemical reduction to the corresponding aldehydes. Electron-donating substituents in the para position inhibit the reaction. It is possible to predict from the pK_a value of the acid or, more accurately, from the polarographic half-wave potential of the corresponding methyl ester whether or not the method is applicable for the preparation of an aldehyde.

The chemical reduction of a carboxylic acid to the corresponding aldehyde generally involves initial formation of a derivative of the acid other than a salt and subsequent reduction of the derivative. Calcium or manganese salts of carboxylic acids can be converted to the aldehydes by pyrolysis in the presence of the corresponding formate salts.[1,2] Similarly, the vapor phase reaction of a mixture of a carboxylic acid and formic acid over TiO_2 or ThO_2 leads to the aldehyde.[3] Although the reduction of carboxylic acids to the aldehydes by $(i\text{-Bu})_2AlH$ has been reported,[4] aluminum and boron hydrides generally reduce acids to the corresponding alcohols. However, acids such as perfluoroaliphatic acids, oxalic acid, or salicylic acid are re-

(1) E. Müller, "Methoden der Organische Chemie" (Houben-Weyl), Vol. VII, Part 1, Georg Thieme Verlag, Stuttgart, 1954, p 277.
(2) P. Mastagli, P. Lambert, and C. Hirigoyen, *C. R. Acad. Sci.*, **248**, 1830 (1959).
(3) P. Sabatier and A. Mailhe, *ibid.*, **154**, 561 (1912).
(4) L. I. Zakharkin and I. M. Khorlina, *Zh. Obshch. Khim*, **34**, 1029 (1964).

duced to the aldehydes by $LiAlH_4$.[5] Lithium in ethylamine reduces aliphatic acids to the corresponding aldehydes[6] and sodium amalgam has been used to reduce aromatic acids to the corresponding aldehydes.[7]

It is generally believed that the electrochemical reduction of aromatic acids leads to the corresponding benzyl alcohol, since the intermediate aldehyde is more easily reduced than the parent acid.[8] There are several reported examples, however, of reductions in which the aldehyde has been trapped to protect it from further reduction. The most widely studied example is the reduction of salicylic acid to salicylaldehyde. In this case, the aldehyde is usually protected by *in situ* formation of the bisulfite addition complex.[9]

$$ArCO_2H \xrightarrow[-H_2O]{2e + 2H^+} ArCHO \xrightarrow[2H^+]{2e} ArCH_2OH$$

The reductions of several heterocyclic carboxylic acids to the corresponding aldehydes have been reported.[10] This is possible because the aldehydes exist in solution partially as the nonreducible hydrated species.

The aldehyde formed on reduction of 2,3-naphtholcarboxylic acid has been trapped with *p*-toluidine to form the insoluble Schiff base, but only in poor yield.[11]

The reduction of benzoic acid to benzaldehyde has been reported to occur in 30–50% yield in an undivided cell using benzene to extract the aldehyde.[12] However, other workers have been unable to reproduce these results.[13] This paper is a report of a simple general method for the electroreduction of aromatic carboxylic acids to the aldehydes and the methods of predicting the applicability of the reaction to a given acid.

Results and Discussion

The results of the attempted electroreduction of various aromatic carboxylic acids to the corresponding aldehydes are shown in Table I. The method (when boric acid is indicated as the buffer) is essentially that described by Mettler[12] except that a divided cell was used, the pH was continually controlled at pH 6 ± 0.2, and ammonium ion was substituted for sodium ion. These changes resulted in a considerable improvement over previously reported results in the initial current efficiency for salicylaldehyde formation. The use of benzene to extract the aldehyde from the catholyte as described by Mettler allows for more convenient recovery of the product than is possible using the bisulfite method of protecting the aldehyde.[9]

The method is limited in general to acids with carboxyl groups directly attached to an aromatic ring, and the current efficiency is poor for compounds with para electron-donating substituents. Of course, substituents more easily reduced than carboxylate, such as nitro groups, would also be reduced.

TABLE I
REDUCTIONS OF VARIOUS CARBOXYLIC ACIDS TO THE ALDEHYDES

Acid	Registry no.	Current efficiency,[a] %	Buffer	pK_a[b]	$E_{1/2}$ vs. sce[c]
Benzoic	65-85-0	55	H_3BO_3	4.20	−2.12[c,d]
Benzoic		8	None		
Benzoic		42	Phosphate		
Salicylic	69-72-7	73	H_3BO_3	3.00	−2.02[d]
Salicylic		Trace	None		
Salicylic		Trace	Phosphate		
p-Hydroxybenzoic	99-96-7	3	H_3BO_3	4.48	−2.32[d]
o-Methoxybenzoic	586-38-9	55	H_3BO_3	4.08	
o-Methoxybenzoic		7	None		
o-Methoxybenzoic		43	Phosphate		
p-Methoxybenzoic	100-09-4	1.75	H_3BO_3	4.47	−2.31[d]
o-Toluic	118-90-1	3	H_3BO_3	3.91	−2.21[c]
p-Toluic	99-94-5	15	H_3BO_3	4.37	−2.20[c,d]
o-Acetoxybenzoic	50-78-2	41	H_3BO_3	3.49	
o-Acetoxybenzoic		1.5	None		
o-Acetoxybenzoic		3.5	Phosphate		
p-Cyanobenzoic	619-65-8	37	H_3BO_3	3.55	
o-Fluorobenzoic	445-29-4	41	H_3BO_3	3.27	
o-Fluorobenzoic		14	None		
o-Fluorobenzoic		46	Phosphate		
Vanillic	121-34-6	5	H_3BO_3	4.48	
Phenylacetic		None	H_3BO_3	4.31	
Phenoxyacetic		None	H_3BO_3	3.17	

[a] To the corresponding aldehyde. [b] Values taken from "Handbook of Tables for Organic Compound Identification," 3rd ed, Chemical Rubber Co., Cleveland, Ohio, 1967. [c] Values determined for the methyl esters in 50% ethanol containing 0.1 *M* $Et_4N^+ClO_4^-$. [d] Values taken from T. Arai, *Nippon Kagaku Zasshi*, **89**, 188 (1968), were converted to the numbers shown by addition of −0.42 V as determined from the two overlapping compounds, methyl benzoate and methyl *p*-toluate.

It is possible to predict the efficiency of the reduction of a given acid to the aldehyde from the pK_a value of the acid. From values shown in Table I one can see that acids with pK_a values greater than 4.40 undergo reduction to the aldehyde with very poor current efficiency.

A more accurate prediction of the result with a given acid may be obtained by the comparison of polarographic half-wave reduction potentials of the corresponding methyl esters (Table I). Thus, if a methyl ester has an $E_{1/2}$ value of −2.20 (*vs.* sce in 50% ethanol containing 0.1 *M* $Et_4N^+ClO_4^-$) or a more negative value, the current efficiency for the reduction of the acid to the aldehyde will be very low.

The assumption is made that the species being reduced is the carboxylic acid, a carboxylate ion pair, or a complexed carboxylate. Free carboxylate anion does

(5) Reference 1, p 303.
(6) A. W. Bergstohler, L. R. Worden, and T. B. Lewis, *J. Org. Chem.*, **28**, 2918 (1963).
(7) H. Weil, M. Traun, and S. Marcel, *Chem. Ber.*, **55**, 2664 (1922).
(8) M. J. Allen, "Organic Electrode Processes," Reinhold, New York, N. Y., 1958, p 71.
(9) (a) J. A. May and K. A. Kobe, *J. Electrochem. Soc.*, **97**, 183 (1950), and references cited therein; (b) K. S. Udupa, G. S. Subramanian, and H. V. K. Udupa, *Ind. Chem.*, **39**, 238 (1963).
(10) (a) H. Lund, *Acta Chem. Scand.*, **17**, 972 (1963); (b) P. E. Iversen and H. Lund, *ibid.*, **21**, 279, 389 (1967); (c) P. E. Iversen, *ibid.*, **24**, 2459 (1970).
(11) N. M. Przhiyalgovskaya, L. N. Lavrishcheva, G. T. Mondodoev, and V. N. Belov, *J. Gen. Chem. USSR*, **31**, 2163 (1960).
(12) C. Mettler, *Chem. Ber.*, **41**, 4148 (1908).
(13) K. S. Tesh and A. Lowy, *Trans. Electrochem. Soc.*, **45**, 37 (1924).

not reduce, as can be determined by the polarography of quaternary ammonium carboxylates.[14]

The reduction normally occurs near the electrode potential at which ammonium ion reduces and it appears that difficultly reducible compounds reduce at more negative potentials than ammonium ion. They cannot compete favorably in the electrode reaction, allowing the majority of the current to be consumed by ammonium ion and proton reduction.

The reduction of ammonium ion causes an operational problem during long-term electrolysis. Ammonium ion is reduced to ammonium amalgam,[15] which slowly decomposes to ammonia and hydrogen, which form a mercury foam on the cathode surface. The foam may be removed physically or by simply stopping the electrolysis for a few minutes, at which time the gases will escape, the mercury surface will return to normal, and the electrolysis can be resumed.

Steric Effects.—One would predict from the pK_a value of *o*-toluic acid that it would be reduced with good current efficiency to the aldehyde. Further, one would predict from Hammett substituent constants that methyl *o*-toluate would be more easily reduced than methyl *p*-toluate.[16] Although neither of these predictions is correct, the relative reduction potential of methyl *o*-toluate does correctly predict the result of the *o*-toluic acid reduction. Apparently the *o*-methyl group sterically inhibits coplanarity between the carboxyl group and the aromatic ring, making the reduction occur at a more negative potential than would be predicted from inductive effects. The carboxylate can be reduced only if π overlap with the aromatic ring can occur, as is shown by the inertness of phenylacetic and phenoxyacetic acids to reduction, even though the magnitude of the inductance is similar to that of reducible acids. Steric inhibition to coplanarity with the ring by *o*-methyl groups has also been shown to occur in other reductions.[16] From the small difference between $E_{1/2}$ values for methyl *o*-toluate and methyl *p*-toluate, less difference in the current efficiencies for the acid reductions would be expected. This may indicate that the species being reduced is more bulky than the methyl ester, *e.g.*, an ion pair with ammonium ion.

Effects of Buffering.—In several examples the reductions were carried out with the boric acid omitted or replaced with a phosphate buffer. From the results (Table I) it is clear that salicylic acid and acetylsalicylic acid are reduced as borate complexes (in agreement with previous results[9]) and the uncomplexed carboxylates are not reduced. None of the other acids tried were particularly sensitive to the type of buffering agent and, therefore, must be reduced as the free acid or an ion pair. In the absence of a buffer the pH at the cathode surface has been shown to be very high.[17] Even under these conditions some aldehyde was formed in most cases, and it is highly unlikely that free carboxylic acid would have been available at the electrode surface. Therefore, the most likely reaction is the reduction of an ion pair, since, as stated previously, the free carboxylate anion is not reducible.

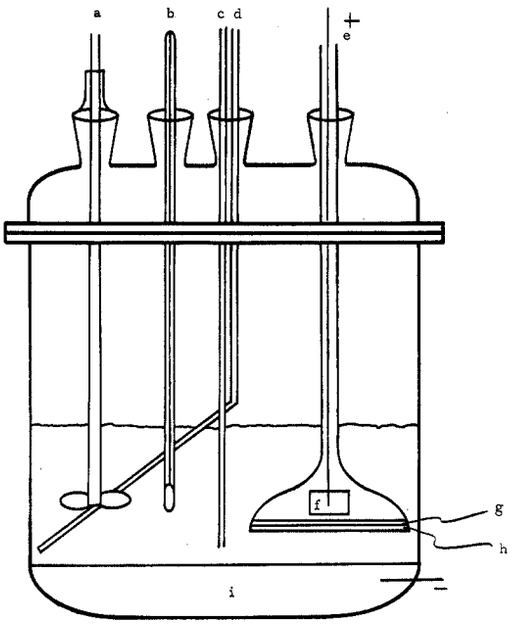

Figure 1.—Electrolysis cell: (a) stirrer; (b) thermometer; (c) entrance for pH meter side stream; (d) exit stream; (e) anode compartment; (f) anode; (g) agar layer; (h) glass frit; (i) Hg pool.

Protection of the Aldehyde.—The efficiency of aldehyde removal by benzene extraction is remarkable. In the case of salicylaldehyde, only about 4% of the alcohol, saligenin, was obtained in a reduction carried out to more than 50% conversion of the acid. Further, the yield of salicylaldehyde based on unrecovered starting material was 80%. The initial reduction product of an aromatic acid is probably the hydrated aldehyde I. Since aromatic aldehydes are known to be

$$\mathrm{ArCO_2H} \xrightarrow[2\mathrm{H^+}]{2\mathrm{e}} \mathrm{ArCOH}(\mathrm{OH},\mathrm{H}) \xrightarrow{-\mathrm{H_2O}} \mathrm{ArCHO}$$

I

reducible, it would seem that any formed at the electrode surface would be immediately reduced to the benzyl alcohol derivative. Thus, apparently the rate of dehydration of I is slow enough to allow the species I to leave the electrode surface. Dehydration in the bulk solution to the aldehyde is followed by rapid extraction into the organic solvent. The fact that a buffer is necessary for the reaction is consistent with the above scheme, since aldehyde hydration reactions are base catalyzed.[18]

Experimental Section

All acids and aldehydes were obtained commercially and used as received. Polarography was carried out with a Sargent XXI polarograph using a conventional H cell with a saturated calomel reference electrode. Gas chromatographic analyses were performed on a Varian Series 1200 chromatograph or an F & M Model 5750 chromatograph, both with flame detectors.

Electrolysis Cell.—The electrolyses were carried out in the apparatus shown in Figure 1. Power was supplied by a Sorensen Nobatron DCR 300-2.5 constant-current power supply. A portion of the catholyte was cycled *via* $^1/_4$-in. polyethylene tub-

(14) In the presence of excess tetraethylammonium hydroxide, benzoate and salicylate show no polarographic reduction waves. Certain substituted benzoates, such as bromobenzoates, are reducible but the substituent is probably being reduced (J. H. Wagenknecht, Ph.D. Dissertation, University of Iowa, Feb 1964).

(15) A. J. Deyrup, *J. Amer. Chem. Soc.*, **56**, 2594 (1934).

(16) P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967.

(17) M. R. Ort and M. M. Baizer, *J. Org. Chem.*, **31**, 1646 (1966).

(18) J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, p 250.

ing to a small, magnetically driven centrifugal pump with a polypropylene head, through a small flask containing pH meter probes and back to the electrolysis cell. The calomel electrode used for pH measurements was separated from the catholyte by an agar plug prepared from 3% agar in 10% aqueous tetramethylammonium chloride. The anode compartment was made from a coarse sintered-glass filter funnel with the walls removed and stem lengthened. A layer of fresh hot solution of 3% agar in 10% aqueous tetramethylammonium chloride was poured onto the anode side of the sintered glass for each experiment. The cell was cooled with an isopropyl alcohol bath to which Dry Ice was added as needed.

General Procedure.—The electrolyses were carried out as follows. Acid (0.15 mol) was neutralized with ammonium hydroxide and diluted to about 250 ml. To this solution was added 18.6 g of boric acid or 20 g of $(NH_4)H_2PO_4$, if a buffer was used. The solution was diluted to 300 ml and adjusted to pH 6 with ammonium hydroxide or dilute hydrochloric acid. This solution, along with 200 ml of benzene, was added to the electrolysis cell. The anolyte consisted of 10% tetramethylammonium chloride with some ammonium hydroxide added to keep the solution basic. The catholyte was stirred vigorously to maintain a good emulsion.

After the solution had been cooled to about 10°, the electrolysis was started with the current set at 0.8 A (current density about 10 mA/cm²). During the electrolysis the temperature was maintained near 10° and the pH was kept at 6 ± 0.2 by the addition of dilute HCl. After 0.5 hr, the electrolysis was stopped, an internal standard was added to the benzene, and that solution was analyzed by gas chromatography for the desired aldehyde. It was on this basis that the current efficiencies shown in Table I were determined.

In a longer experiment using salicylic acid with boric acid present, the electrolysis was carried out at 1.5 A for 5 hr. After each hour, the mercury pool was replaced because of the large amount of mercury foam which had formed on the surface.

Analysis.—After the electrolysis, the benzene was separated and analyzed for salicylaldehyde as below. The aqueous catholyte was divided into two equal portions. One-half was acidified to pH 1 with concentrated HCl and extracted with ether. Gas chromatographic analysis of the ether solution for saligenin indicated that a 4% current efficiency to saligenin was obtained. The other portion of the catholyte was taken to pH 9 with NaOH, diluted, and analyzed for salicylate with a salicylate ion selective electrode[19] by the known addition technique[20] and comparing to known solutions containing approximately the same composition. Of the initial salicylic acid, 90% was accounted for either as unreacted salicylic acid, salicylaldehyde (80% yield, 50% current efficiency), or saligenin.

The analyses of the aldehydes except for hydroxy aldehydes were carried out on a 10 ft × 1/8 in. gas chromatography column packed with 10% Carbowax 20M on Chromosorb G using biphenyl or naphthalene as internal standards.

Salicylaldehyde, saligenin, *p*-hydroxybenzaldehyde, and vanillin were treated in benzene (or ether) solution with Regisil [bis(trimethylsilyl)trifluoroacetamide] and then analyzed by gas chromatography on a 10 ft × 1/8 in. column packed with 10% SE-52 on Chromosorb W using naphthalene or biphenyl as the internal standards.[21]

Acknowledgment.—The author wishes to thank Mr. W. O. Jackson for technical assistance and Drs. M. M. Baizer and D. A. Tyssee for helpful discussions.

(19) W. M. Haynes and J. H. Wagenknecht, *Anal. Lett.*, **4**, 491 (1971).
(20) Orion Newsletter, July 1969, p 9.
(21) Since this paper was submitted, an article has appeared [J. A. Harrison and D. W. Shoesmith, *J. Electroanal. Chem.*, **32**, 125 (1971)] showing significant improvements in the yields of aldehydes in the reduction of aromatic acids by Udupa's method[4b] (rotating Cu amalgam cathode). This was accomplished by replacing metal ions with tetramethylammonium ions and by adding ethanol to the catholyte.

Exchange of Aryl Ligands to Polyvalent Iodine[1]

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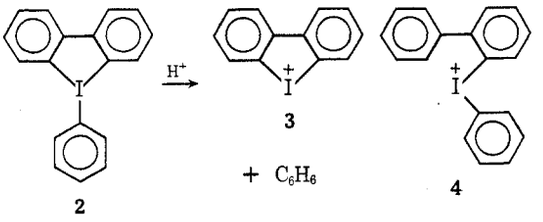
By treatment with aryllithium reagents (RLi) and then acid, diaryliodonium salts ($Ar_2I^+X^-$) have been converted to ArI^+X^- and $R_2I^+X^-$. With [RLi]/[Ar_2I^+] near unity, a triaryliodine can be isolated. The product ratio from its acid cleavage reflects the relative susceptibility of Ar and R to protodeiodination and the selectivity of the reagent. Results include cases where Ar_2 = 2,2′-biphenylene (*i.e.*, Ar_2I^+ is the dibenziodolium ion) and R = C_6H_5, and where Ar = 4-chlorophenyl and R = C_6H_5. With [RLi]/[Ar_2I^+] > 1, aryl groups can be exchanged through three- and four-coordinated iodine intermediates, such as $Ar_2R_2I^-Li^+$. Treatment of the reaction mixture with acid gives iodonium salts whose amounts depend on the equilibria and on the cleavage ratios. Successful replacements include 4-ClC_6H_4 by C_6H_5 and C_6H_5 by 4-$(CH_3)_2NC_6H_4$ and by 2,2′-biphenylene.

Wittig and Clauss[2] reported the formation of the unstable triphenyliodine (**1**) by the addition of 1 equiv of phenyllithium solution to an ether suspension of a diphenyliodonium halide at −80°. Similarly, when a dibenziodolium halide **3** was treated with phenyllithium at 0°, a more stable triaryliodine, 5-phenyl-5*H*-dibenziodole (**2**), was produced.[3,4] Treatment of triaryliodines **1** and **2** with acids had been reported to regenerate the starting iodonium salts.[2,3] However, in a recent investigation of the acid cleavage of 5-phenyl-5*H*-dibenziodole (**2**) we found that, in addition to the starting cyclic dibenziodolium salt (**3**), a new acyclic 2-



biphenylylphenyliodonium salt (**4**) was also formed.[1] The dependence of the product distribution on the protonic or Lewis acid used has been reported.[1]

We should now like to note that this two-step process, formation of a triaryliodine and its cleavage by acid, may be used to replace one aryl group with another in a

(1) (a) Preceding paper: F. M. Beringer and L. L. Chang, *J. Org. Chem.*, **36**, 4055 (1971). (b) Taken from the dissertation of Lydia L. Chang submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry), 1971. (c) Supported by National Institutes of Health, 1968–1969, through Grant No. 5-SO5-FR-07063-04.
(2) G. Wittig and K. Clauss, *Justus Liebigs Ann. Chem.*, **578**, 136 (1952).
(3) K. Clauss, *Chem. Ber.*, **88**, 268 (1955).
(4) Diphenyliodonium chloride and *n*-butyllithium form an unstable trivalent organoiodine which decomposes in solution at approximately −40°: F. M. Beringer, J. W. Dehn, Jr., and M. Winicov, *J. Amer. Chem. Soc.*, **82**, 2948 (1960).