

over a period of 5 min a solution of 5.22 g (0.022 mol) of acetone 2,4-dinitrophenylhydrazone in 60 ml of chloroform. The resulting orange mixture was stirred and heated under reflux for an additional 30 min prior to being cooled and poured into water. The suspension was filtered by suction and the chloroform solution was separated from the filtrate. The aqueous phase was extracted with a 100-ml portion of chloroform and the combined chloroform extracts were washed once with 5% sodium bicarbonate and then twice with water. The dried extract was concentrated under reduced pressure to yield an orange oil which was chromatographed on a column (25 × 2.5 cm diameter) of silica gel. Elution with 4:1 hexane-benzene gave an orange solid which, on recrystallization from methanol, afforded 0.88 g (16%) of azo fluoride 1, having the properties recorded in Tables I and II.

B. 2-Acetoxy-2-(2,4-dinitrophenylazo)propane (1a).—Continued elution with pure benzene of the column from which azo fluoride 1 was obtained, as described above, gave a yellow solid which, on recrystallization from methanol, afforded 3.48 g (53%) of azo acetate 1a, displaying strong peaks in the ir (CCl₄) at 1745, 1600, 1365, 1345, 1245, 1190, and 1155 cm⁻¹. Additional data are given in Tables I and II. A mixture melting point determination and ir spectral comparison showed 1a to be identical with an authentic specimen.³

Reaction of Lead(IV) Diacetate Difluoride with 2-Butanone Phenylhydrazone. Formation of 2-Fluoro-2-phenylazobutane (3) and 2-Acetoxy-2-phenylazobutane (3a).—In a 300-ml, heavy-walled polyethylene jar sealed with a cap holding a drying tube filled with calcium chloride, a stainless steel dial thermometer, and an addition tube of polyethylene connected to a dropping funnel were placed 26.04 g (0.072 mol) of lead(IV) diacetate difluoride and 50 ml of chloroform. After the magnetically stirred suspension had been cooled to 0° in an ice bath, a solution of 11.60 g (0.072 mol) of 2-butanone phenylhydrazone in 15 ml of chloroform was added over a period of 30 min in order to maintain the temperature as close as possible to 0°. The mixture was stirred in the ice bath for an additional 30 min and the resulting amber suspension was then poured into water. The white solid was removed by suction filtration and the chloroform layer was separated from the filtrate. The aqueous layer was extracted with a 100-ml portion of chloroform and the combined chloroform extracts were washed once with 5% sodium bicarbonate and then twice with water. The dried extract was concentrated under reduced pressure to give a red oil which, on distillation under reduced pressure through a semimicro column, gave two main fractions.

Fraction 1, a yellow oil, was identified as azo fluoride 3, yield 2.23 g (17%), bp 65–66° (1.25 mm). Some additional properties are indicated in Tables I and II.

Fraction 2, an orange oil, was identified as azo acetate 3a, yield 6.70 g (42%), bp 102–103° (1.25 mm), *n*_D²⁰ 1.5142 (lit.³ *n*_D²⁰ 1.5141). Its ir spectrum (neat) was indistinguishable from that of an authentic sample.³

Reaction of 2-Acetoxy-2-(2,4-dinitrophenylazo)propane (1a) with Hydrogen Fluoride. Formation of 2-Fluoro-2-(2,4-dinitrophenylazo)propane (1).—To 0.50 g (1.69 mmol) of azo acetate 1a in a polyethylene test tube cooled in a Dry Ice-acetone bath was added 1.0 ml of liquid hydrogen fluoride. The brown suspension was stirred with a nickel spatula for 2 min and then a large excess of potassium fluoride was added. The reaction vessel was removed from the cooling bath and after standing at room temperature for 15 min the mixture was eluted with ether. The ether extract was washed once with 5% sodium bicarbonate and then twice with water. Evaporation at reduced pressure of the dried ether solution gave an orange oil which was chromatographed on a column (20 × 1.2 cm diameter) of silica gel with 6:1 benzene-hexane as eluent. An orange solid was thus obtained which was recrystallized from methanol to give 0.26 g (60%) of azo fluoride 1, mp 51–52°. Compound 1 was shown by mixture melting point determination and ir spectral comparison to be identical with an authentic sample prepared above by reaction of lead(IV) diacetate difluoride with acetone 2,4-dinitrophenylhydrazone.

1-Fluoro-1-(2,4-dinitrophenylazo)cyclohexane (4).—Treatment of 0.50 g (1.49 mmol) of 1-acetoxy-1-(2,4-dinitrophenylazo)cyclohexane (4a) with liquid hydrogen fluoride for 5 min by the procedure used above to convert azo acetate 1a into azo fluoride 1 afforded an orange solid which was recrystallized from methanol, yield 0.29 g (66%), mp 79–80°. It was identical in all respects with a sample of 4 prepared by fluorination of cyclohexanone

2,4-dinitrophenylhydrazone with lead(IV) diacetate difluoride (Table I).

Registry No.—Lead(IV) diacetate difluoride, 20706-24-5; 1, 23386-00-7; 1a, 23386-01-8; 2, 23386-02-9; 2a, 23386-03-0; 3, 23383-04-1; 3a, 23386-05-2; 4, 23386-06-3; 4a, 23386-07-4; 5, 23386-08-5; 5a, 14803-32-8.

Selective Electrochemical Reduction of Polyfunctional Molecules

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It has been recognized for a number of years that controlled-potential electrolysis, employing as it does constant electrode potential in order to discriminate between two or more electrode processes,¹ provides a considerably more selective method of effecting electrochemical reaction than does the method of constant-current electrolysis used in the older literature.² Controlled-potential electrolysis is in fact now widely used both in coulometric analysis of mixtures of reducible species³ and in preparative-scale electrochemical synthesis. In most cases the latter application involves preparation of an electrolysis product in sufficient quantities for characterization by the usual chemical and spectroscopic methods, in order to test or confirm an electrode mechanism proposed, *e.g.*, from voltammetric data.⁴ Despite the common use of controlled-potential electrolysis for the latter purpose, there are surprisingly few reports of its use for the specific purpose of carrying out oxidations or reductions not possible by the usual chemical means. This is unfortunate, for even a cursory examination of the organic polarographic literature⁵ will reveal the possibility of many selective electrochemical reductions which would be either impossible or very difficult using the conventional reducing agents of organic chemistry. The principal criterion for the successful application of the electrochemical method is simply that, when a molecule contains two or more reducible functions, the electrode process of interest must be easier than any others by at least 0.2 V; if so, electrolysis at a potential corresponding to the first process will permit clean conversion into the product of this reduction process and no other.⁶ The first instance (and still one of the best examples) where this principle was taken advantage of for explicitly synthetic purposes was reported by Lingane, Swain, and Fields.⁷

(1) J. J. Lingane, "Electroanalytical Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1958.

(2) S. Swann, Jr., in "Technique of Organic Chemistry," Vol. 2, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p 385.

(3) G. W. C. Milner and G. Phillips, "Coulometry in Analytical Chemistry," Pergamon Press, London, 1967.

(4) L. Meites, "Polarographic Techniques," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 10.

(5) (a) D. J. Pietrzyk, *Anal. Chem.*, **40**, 194R (1968); **38**, 278R (1966).

(b) P. Zuman, "Organic Polarographic Analysis," Pergamon Press, London, 1964.

(6) L. Meites in "Technique of Organic Chemistry," 3rd ed, Vol. 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., p 3281 ff.

(7) J. J. Lingane, C. G. Swain, and M. Fields, *J. Amer. Chem. Soc.*, **65**, 1348 (1943).

TABLE I^a
HALF-WAVE POTENTIALS FOR REPRESENTATIVE
ORGANIC COMPOUNDS^b

Compd	$-E_{1/2}$, V
RC≡CR, R ₂ C=CR ₂ , RCN, RCO ₂ R, RCl (R = alkyl)	>2.6 ^c
Acetone	2.46
Acetophenone	2.42
Bromobenzene	2.32
Ethyl bromide	2.27
Benzonitrile	2.26
Ethyl benzoate	2.14
Benzyl chloride	1.94
Ethyl iodide	1.67
Iodobenzene	1.62
Benzyl bromide	~1.3

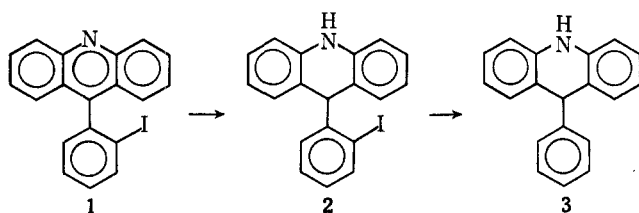
^a M. V. Stackelberg and W. Stracke, *Z. Elektrochim.*, **53**, 118 (1959). ^b Half-wave potentials are reported relative to the saturated calomel electrode; the solvent was 75% dioxane containing tetraethylammonium bromide as supporting electrolyte. ^c Material not reduced before the solvent decomposition potential (-2.6 V) is reached.

TABLE II
SELECTIVE ELECTROCHEMICAL REDUCTIONS^a

Starting material ^b	Product	Yield, % ^c
<i>p</i> -Bromo-2-chloroethylbenzene	2-Chloroethylbenzene	99
<i>m</i> -Bromoacetophenone	Acetophenone	94
<i>p</i> -Bromiodobenzene	Bromobenzene	98 (94) ^d
<i>p</i> -Bromo- γ -chlorobutyrophenone	γ -Chlorobutyrophenone	96

^a Electrochemical reductions were carried out at 25° in dimethylformamide containing 0.1 *M* tetraethylammonium bromide. ^b Starting materials were purified by preparative vpc before use. ^c Yields were determined by direct gas chromatographic analysis of electrolysis mixtures. ^d Yield in parentheses is that for a preparative-scale electrolysis.

It was desired to convert 9-(*o*-iodophenyl)acridine (1) into the corresponding acridane 2, but every chemical reducing agent tried effected simultaneous hydrogenolysis of the iodine atom to afford not 2, but 3.



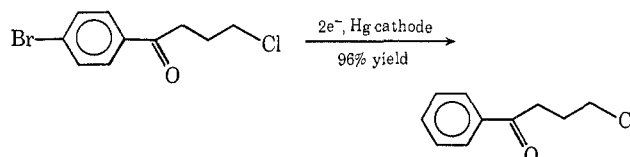
Acridine 1 has, however, two polarographic waves in alkaline ethanol; the first, at -1.32 V *vs.* sce, corresponds to the desired reduction to 2, and the second, at -1.62 V, corresponds to conversion into 3. The two electrode processes are resolved sufficiently (0.3 V) to permit application of the electrochemical method. Electrolysis at -1.37 V readily afforded 2 in 90% (isolated) yield, and, furthermore, reduction of 2 at -1.70 V afforded 3 in 95% yield. Acridine 1 could thus be converted into either 2 or 3 by appropriate choice of cathode potential.

Polarographic half-wave potential data are available for thousands of compounds, primarily from the analytical literature.⁵ An abbreviated list, adequate for suggesting many useful synthetic applications of controlled-potential electrolysis, is given in Table I. Compounds are listed in increasing ease of reducibility as one proceeds down the table. It should be pointed out that

the potential at which a given solvent-electrolyte system is itself reduced places a natural limit upon the range of reductions which may be effected in that solvent. Unconjugated olefins, acetylenes, alkyl chlorides nitriles, and esters, for example, are not normally electrochemically reducible in most solvents, and ketones are only difficultly reducible. On the other hand, alkyl and aryl bromine and iodine are all easily reduced electrochemically under conditions where the preceding groups are stable against reduction. This order of ease of reduction, which differs in a number of respects from that observed with typical organic reducing agents such as complex metal hydrides, dissolving metals, catalytic hydrogenation, etc.,⁸ may be put to good synthetic advantage. We have utilized the order of ease of reductions implied by Table I to effect in high yield a number of selective reductions, any one of which would have been difficult or impossible by other methods (Table II). No attempt was made to compile an exhaustive list of selective reductions, since, while many

other interesting conversions are clearly implied in the data of Table I, further applications would be straightforward.

The selective reduction of *p*-bromo- γ -chlorobutyrophenone, containing three potentially reducible functions, is a particularly striking demonstration of the utility of the electrochemical method.⁹



It should be noted that the electrochemical reduction of alkyl halides does *not* suffer, as has been suggested,¹⁰ from the disadvantage that there are involved strongly basic conditions which preclude the use of base-sensitive reactants or products. Carbanions are indeed generated during the electrolysis of alkyl halides, but they are rapidly deactivated *via* Hoffmann dealkylation of the tetraalkylammonium salts used as supporting electrolyte; consequently, a much less basic tertiary amine is generated. In this connection, it is interesting to

(8) (a) R. L. Augustine, "Reduction," M. Dekker, Inc., New York, N. Y., 1968; (b) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965.

(9) Although bromobenzene and acetophenone differ in reduction potential by less than the above stated requisite of 0.2 V, a smaller difference can be tolerated when the first reduction is irreversible, as it is for alkyl halides.

(10) G. L. Grady and H. Kuivila, *J. Org. Chem.*, **34**, 2014 (1969).

note that *p*-bromoacetophenone is converted into acetophenone in only 13% yield using tri-*n*-butyltin hydride,¹⁰ while *m*-bromoacetophenone is converted into acetophenone in 94% yield electrochemically, without appreciable base-catalyzed aldolization. The electrochemical method is, however, more difficult to scale up for large-scale preparations. For the occasional highly base-sensitive system, one may, furthermore, take advantage of the pH independence of the electrochemical reduction of alkyl halides¹¹ by purposely adding an acid (phenol or even mineral acid¹²) to the mixture to protonate the carbanion as formed.

Experimental Section

Apparatus and Chemicals.—Dimethylformamide was refluxed over calcium hydride [70° (0.1 mm)] for 1 hr, followed by distillation *in vacuo* through a 10 × 300 mm glass helix packed column. Tetraethylammonium bromide was recrystallized from an ethanol ether mixture and dried *in vacuo*. Controlled-potential electrolyses were carried out with the aid of a potentiostat based upon a Kepco KS-120-2.5 programmable power supply.¹³

Electrolyses.—A modified polarographic H cell was used for small-scale electrolyses; the dme was replaced by a mercury pool, for which electrical contact was maintained *via* a platinum contact piercing the cell wall. A mechanical stirrer and Cd(Hg)-CdCl₂ reference¹⁴ (isolated by a methyl cellulose plug¹⁵) were positioned close to the mercury surface. One side of the cell contained the catholyte [5 ml of a solution of the organic substrate (10⁻² M) and Et₄NBr (10⁻¹ M) in DMF, and the other side of the cell contained a silver anode in a solution of 10⁻¹ M Et₄NBr in DMF. A methyl cellulose plug¹⁵ separated the two sides of the cell. Electrochemical reductions were carried out upon samples freshly purified by preparative glpc. After electrolysis, the contents of the cell were analyzed directly by vpc (Varian Aerograph Model 1740). Preparative electrolysis of *p*-iodobromobenzene was carried out in 90% ethanol containing 0.1 M tetraethylammonium bromide in a large crystallizing dish containing a platinum anode, mercury pool cathode, Cd(Hg)-CdCl₂ reference electrode, and mechanical stirrer. Hydrazine hydrate was added as the anodic depolarizer; its oxidation to nitrogen at the anode also generates protons to prevent the solution from becoming basic. From 28.3 g (0.1 mol) of *p*-iodobromobenzene was isolated, after dilution with water, extraction with pentane, and distillation of the solvent, 14.7 g (94%) of bromobenzene, homogeneous by vpc.

***p*-Bromo-2-chloroethylbenzene.**—*p*-Bromo-2-phenylethanol¹⁶ was prepared through lithium aluminum hydride reduction of *p*-bromophenylacetic acid. A solution of 20.0 g each of the alcohol and thionyl chloride was refluxed overnight. Thionyl chloride was then removed with warming at the rotary evaporator. Distillation afforded *p*-bromo-2-chloroethylbenzene: yield 15 g (65%); bp 70° (0.15 mm); nmr (CCl₄) τ 2.73 and 3.07 (AB pattern, *J* = 8.5 Hz, area 4), 6.50 (t, *J* = 6.5 Hz, area 2), and 7.07 (t, *J* = 6.5 Hz, area 2).

Anal. Calcd for C₈H₈ClBr: C, 43.88; H, 3.62. Found: C, 43.61; H, 3.51.

Registry No.—*p*-Bromo-2-chloroethylbenzene, 23386-17-6.

Acknowledgment.—Financial support was provided by the National Science Foundation and the Petroleum Research Fund of the American Chemical Society.

(11) See footnote a, Table I.

(12) A. J. Fry and R. H. Moore, *J. Org. Chem.*, **33**, 1283 (1968).

(13) P. Birman, "Power Supply Handbook," Kepco Inc., Flushing, N. Y., 1965, p 129.

(14) L. W. Marple, *Anal. Chem.*, **39**, 844 (1967). This electrode is ca. -0.9 V relative to sce.

(15) G. Dryhurst and P. J. Elving, *ibid.*, **39**, 607 (1967).

(16) D. Sontag, *Ann. Chim. (Paris)*, **1** (11), 359 (1934).

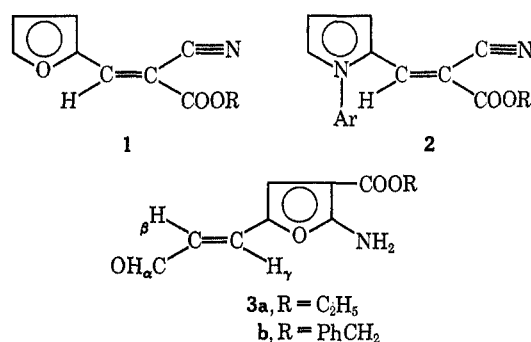
Base-Catalyzed Reactions of α-Cyano-β-furylacrylic Esters

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The ring-opening reactions of the furan derivatives with ammonia and amines have been extensively investigated by a number of authors.² Leditschke³ reported that the reaction of α-cyano-β-furylacrylic esters (1) with primary arylamines afforded α-cyano-1-aryl-2-pyrroleacrylic esters (2). However, we have found that 1, when treated with morpholine instead of the primary arylamines, gives rise to an unexpected colored product. We have shown this product to have the structure γ-(4-alkoxycarbonyl-5-aminofuryl)-acrolein (3).



The product 3a obtained from ethyl α-cyano-β-furylacrylate (1, R = C₂H₅) and morpholine, was recrystallized from chloroform as yellowish green needles, mp 174–175°, having a molecular ion peak at *m/e* 209, and a molecular formula of C₁₀H₁₁NO₄. When treated with 2,4-dinitrophenylhydrazine and semicarbazide, 3a gave the corresponding hydrazone 4 and semicarbazone 5, respectively, and when treated with fuchsin reagents, showed a positive test for aldehyde. All attempts to acetylate 3a were unsuccessful, and catalytic hydrogenation led to a colorless polymer.

The ir spectrum of 3a (CHCl₃) revealed the disappearance of the cyano group. The NH₂ and ester C=O stretching frequencies appeared at 3508 and 3382 and at 1672 cm⁻¹, respectively, comparable with those of ethyl 5,7-dimethyl-2-amino-3-benzofuroate (3480 and 3346, and 1679 cm⁻¹).⁴ The aldehydic CH stretching bands are clearly observed at 2818 and 2730 cm⁻¹.

The nmr spectrum (deuterated DMSO) showed that morpholine used in the reaction is not entering into the reaction product. The presence of the CH=CHCHO system is supported by the fact that the two olefinic protons and aldehydic proton constitute the three spin AMX pattern. A rather large coupling constant between the two olefinic protons suggests the *trans* configuration about the C=C bond. The mass spec-

(1) Chemical Laboratory, Department of Education, University of Utsunomiya, Japan.

(2) P. Bosshard and C. H. Eugster, *Advan. Heterocycl. Chem.*, **7**, 378 (1966).

(3) H. Leditschke, *Chem. Ber.*, **85**, 483 (1952).

(4) J. Derkosch and I. Specht, *Monatsh. Chem.*, **92**, 542 (1961).