[Contribution from the Chemical Laboratory of the University of Kansas]

Anodic Reductions. VII. Reduction of Nitrosobenzene, Azoxybenzene, and Azobenzene by Lower Valent Aluminum Anodically Generated

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The "anodic reductions" by lower valent aluminum of nitrosobenzene, azoxybenzene, and azobenzene in lithium chloride-pyridine solution have been studied. In each case, a two-electron reduction has been observed. The results have been compared with those obtained in an analogous investigation with unipositive magnesium, anodically generated, as reducing agent.

Considerable experimental evidence for the generation of lower valent aluminum by anodic oxidation of the metal has appeared in the literature. Early experimenters[1,2] noted the evolution of hydrogen at the anode in the electrolysis of aqueous sodium chloride between aluminum electrodes; moreover, the aluminum anode dissolved with a current efficiency significantly greater than 100% on the assumption of oxidation to the tripositive state. Recently, persuasive additional support for the anodic generation of lower valent aluminum in aqueous salt solutions has been reported.[3] It was demonstrated that when a flowing anolyte consisting of sodium chloride or nitrate solution was passed over an aluminum rod serving as anode and then into a solution of an oxidizing agent, *e.g.*, permanganate or silver ion, contained in a separate vessel, reduction of the oxidant occurred, permanganate to manganese dioxide and silver ion to metallic silver. The only logical interpretation of the occurrence of reduction at a distance from the anode would appear to be in terms of the formation of lower valent aluminum as a primary anodic process.

Substantial evidence for the anodic generation of lower valent aluminum in non-aqueous solvents has also been reported.[4-8]

In this laboratory we have been concerned for some time with the "anodic reduction" of organic compounds by means of lower valent species of active metals.[9-15] Of specific significance to the current paper is the reduction of benzophenone to the conjugate bases of benzhydrol and benzopinacol by lower valent aluminum anodically generated in anhydrous pyridine.[15] We now report that nitrosobenzene, azoxybenzene, and azobenzene can also be reduced analogously. The major objective of the study herein reported is to compare the results with those obtained when the same compounds were reduced by anodically generated unipositive magnesium.[13]

In a typical electrolysis in anhydrous pyridine in which the anolyte contained nitrosobenzene and the electrolyte consisted of a saturated solution of lithium chloride, the aluminum anode entered solution with an initial mean valence number (V_i) of 1.26. After hydrolysis of the anolyte following electrolysis, azoxybenzene was isolated in an amount which exceeded slightly the theoretical based on oxidation by nitrosobenzene of aluminum from its initial mean valence state to the familiar tripositive state.

Since no evidence was found that any substantial amount of the reduction product arose by the action of some reducing species which had migrated from the catholyte, reduction in the anolyte presumably occurs through the agency of lower valent aluminum generated anodically. In view of the electronic configuration of the aluminum atom and the results of previous investigations[3,16-18] of the anodic oxidation of aluminum and other metals, it seems reasonable to suggest that unipositive aluminum is formed as the primary anodic

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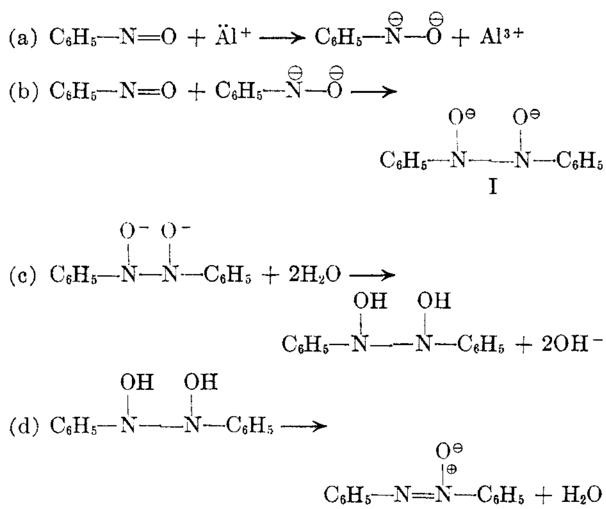
process. The observed V_i value arises as a result of the relative rates of a number of competing reactions: (1) oxidation of the unipositive aluminum by loss of electrons in a stepwise manner to the anode, and (2) oxidation of lower valent aluminum (Al^+, Al^{2+}) by nitrosobenzene.

The isolation of azoxybenzene as the sole reduction product from the anolyte hydrolyzate[19] may be reasonably explained. Azoxybenzene is believed to be formed as shown below when unipositive aluminum is the reducing agent:



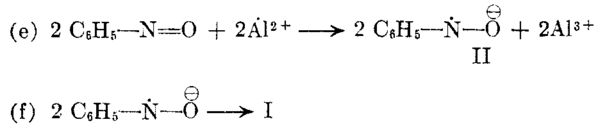
$$\text{(a)}\ C_6H_5{-}N{=}O + \ddot{A}l^+ \longrightarrow C_6H_5{-}\overset{\ominus}{\dot{N}}{-}\overset{\ominus}{O} + Al^{3+}$$

$$\text{(b)}\ C_6H_5{-}N{=}O + C_6H_5{-}\overset{\ominus}{\dot{N}}{-}\overset{\ominus}{O} \longrightarrow \underset{\text{I}}{C_6H_5{-}\overset{O^\ominus}{\overset{|}{N}}{-}{-}\overset{O^\ominus}{\overset{|}{N}}{-}C_6H_5}$$

$$\text{(c)}\ C_6H_5{-}\overset{O^-}{\overset{|}{N}}{-}\overset{O^-}{\overset{|}{N}}{-}C_6H_5 + 2H_2O \longrightarrow C_6H_5{-}\overset{OH}{\overset{|}{N}}{-}{-}\overset{OH}{\overset{|}{N}}{-}C_6H_5 + 2OH^-$$

$$\text{(d)}\ C_6H_5{-}\overset{OH}{\overset{|}{N}}{-}{-}\overset{OH}{\overset{|}{N}}{-}C_6H_5 \longrightarrow C_6H_5{-}N{=}\overset{O^\ominus}{\overset{|}{\overset{\oplus}{N}}}{-}C_6H_5 + H_2O$$

When bipositive aluminum functions as the reducing agent, intermediate I is thought to arise by the reactions



$$\text{(e)}\ 2\ C_6H_5{-}N{=}O + 2\dot{A}l^{2+} \longrightarrow 2\ \underset{\text{II}}{C_6H_5{-}\dot{N}{-}\overset{\ominus}{O}} + 2Al^{3+}$$

$$\text{(f)}\ 2\ C_6H_5{-}\dot{N}{-}\overset{\ominus}{O} \longrightarrow \text{I}$$

Evidence for the formation of intermediate I comes from the fact that *during the course of electrolysis no inorganic oxide is formed in the anolyte.* In one experiment, the anolyte immediately following electrolysis was passed through a sintered glass filter funnel. No residue was left behind on the disk. Since metal oxides which might have been formed (lithium oxide and aluminum oxide) are insoluble in pyridine, the absence of precipitate in the anolyte definitely shows that no metal oxide was produced during electrolysis. Thus, the departure of oxygen occurred during hydrolysis.

It is of interest that "anodic reduction" of nitrosobenzene by unipositive magnesium gives (after hydrolysis) both azoxybenzene and azobenzene and that *metal oxide is formed in the anolyte during electrolysis.* The latter observation explains why azobenzene, a reduction product of azoxybenzene, is formed when unipositive magnesium acts as the reducing agent toward nitrosobenzene. The fact that intermediate I does not lose oxide ion during electrolysis when aluminum is the anode and lithium chloride the electrolyte precludes the production of azobenzene in this experiment.

A control experiment showed that nitrosobenzene dissolved in a saturated solution of lithium chloride in pyridine did not corrode an aluminum rod. However, after electrolysis the anolyte attacked aluminum very slowly; in one experiment, it was observed that four milligrams of aluminum were dissolved in a period of twenty-four hours. This is to be contrasted with the behavior of a similar anolyte remaining after anodic oxidation of magnesium.[13] In this case, a magnesium rod was corroded at a rapid rate. Furthermore, the original electrolytic solution containing nitrosobenzene attacked massive magnesium slowly. These results may reasonably be explained by the fact that aluminum is inherently less reactive than magnesium and the assumption that the concentration of the radical-ion II, the only species formed during electrolysis that is capable of attacking aluminum, is always small in electrolyses where aluminum functions as anode; that is, it is thought that reactions (a) and (b) above account for the formation of a much larger fraction of I than do reactions (e) and (f).

With azoxybenzene present in the anolyte, aluminum entered solution with V_i values in the range 2.61–2.68 and the reduction product isolated from the anolyte hydrolyzate was azobenzene in amounts corresponding to the oxidation by azoxybenzene of the metal from the observed V_i to the +3 state. Prior to hydrolysis, the anolyte solution was clear, an excellent indication that no metal oxide was formed during electrolysis. Control and corrosion experiments showed that neither before nor after electrolysis did the anolyte corrode massive aluminum. It is interesting to note that "anodic reduction" of azoxybenzene by unipositive magnesium also yielded azobenzene as the sole reduction product.[13]

Electrolyses between aluminum electrodes carried out in saturated lithium chloride–pyridine solutions containing azobenzene gave inconsistent V_i values, some normal, *i.e.*, 3, and others below 3. In an experiment in which the V_i value was 2.67, hydrazobenzene was isolated from the anolyte hydrolyzate in 68% yield. A small amount of 4,4′-dipyridyl was also obtained. Evidence is presented in the Experimental section that the dipyridyl arises at least in part from the conjugate base of tetrahydro-4,4′-dipyridyl which migrates from the catholyte compartment of the cell. This conjugate base is frequently formed in the catholyte during electrolyses in pyridine.[9,10] Hydrazobenzene, as would be expected, was also the sole product of the "anodic reduction" of azobenzene by unipositive magnesium.[13]

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(19) In one experiment a trace of azobenzene was obtained in addition to the major reduction product azoxybenzene.

Although detailed mechanisms for the formation of azobenzene from azoxybenzene and of hydrazobenzene from azobenzene have not been presented, it is visualized that these two-electron reductions, like that of nitrosobenzene pictured in equations (a) through (f), occur through the agency of lower valent aluminum.

EXPERIMENTAL

Materials. The 10 mm. aluminum rod from which all electrodes were cut was of 99.98% purity and was furnished by the Aluminum Company of America. The lithium chloride employed as electrolyte was Baker and Adamson reagent grade. Pyridine, Fisher analytical reagent, was fractionally distilled from sodium and stored over barium oxide. Nitrosobenzene, azoxybenzene, and azobenzene were prepared and purified as described in a previous communication.[13]

Apparatus and procedure. The apparatus for carrying out electrolyses has been described previously.[15] All electrolyses were carried out at a constant temperature of 39.5 ± 0.5°.

The aluminum electrodes were cleaned in 10% sodium hydroxide solution, then washed with distilled water and dried in an oven at 110°. A saturated solution of lithium chloride in pyridine was made up and 50 ml. added to each compartment of the electrolytic cell. A weighed quantity of organic additive was then dissolved in the anolyte and the system was swept out with pure, dry nitrogen. Electrolysis was effected under an atmosphere of this gas. The conditions of electrolysis (current density, cell voltage, and duration) are specified in the appropriate places for the individual experiments. After electrolysis, the electrodes were cleaned with ethanol and distilled water and then dried at 110°.

From the loss in weight of the anode during electrolysis and the quantity of current passed through the cell the *initial mean valence number*, V_i, with which the aluminum entered solution was calculated.

$$V_i = \frac{\text{wt. of Ag deposited in coulometer} \times 26.97}{107.88 \times \text{wt. of Al lost from anode}}$$

Electrolyses with nitrosobenzene as additive. Two electrolyses in each of which the anolyte contained 4.000 g. of nitrosobenzene were carried out at an initial anodic current density of 0.002 amp. per cm.^{2} and a cell voltage of 150 V. The V_i values obtained were 1.09 (25 hr.) and 1.26 (10 hr.).

After the electrolysis in which the V_i value was 1.26, the dark anolyte was hydrolyzed with ice water and acidified with hydrochloric acid. The hydrolyzate was extracted continuously with petroleum ether for 24 hr. and then with ethyl ether for an additional 24 hr. Distillation of the organic solvents gave, respectively, 0.6662 g. and 0.4127 g. of black residue. The aqueous phase left after extraction was made basic by addition of sodium hydroxide, and extraction with ether gave a small quantity of brown oil. The three extracts noted above were combined and subjected to chromatographic separation on alumina. The mixture was placed on the column in petroleum ether solution and the column was developed by means of the same solvent. Elution, first with petroleum ether, then with ethyl ether–petroleum ether (1:9), gave 0.4426 g. of pure azoxybenzene, m.p. 35–36°, and 0.1008 g. of slightly impure compound, m.p. 33–34°. The infrared spectrum of the first fraction taken in 10% chloroform solution was identical with that of an analogous solution of authentic azoxybenzene, and the spectrum of the second fraction was nearly identical with that of the known.

Since the reduction of nitrosobenzene to azoxybenzene represents a two-electron process, the following equation was employed to calculate the theoretical yield of the reduction product.

$$\text{Theoretical yield of azoxybenzene} = (3 - V_i) \times \frac{\text{g. of Al dissolved}}{26.97} \times \frac{\text{mol. wt. of azoxybenzene}}{2}$$

The theoretical yield of azoxybenzene was 0.4752 g.

In addition to the reduction product, appreciable tarry material was found in the anolyte. This undoubtedly arose from decomposition of nitrosobenzene.

Electrolyses with azoxybenzene as additive. Two electrolyses in each of which the anolyte contained 3.000 g. of azoxybenzene were carried out at an initial current of 0.014 amp. and a cell voltage of 150 V. The V_i values obtained after electrolysis for 25 hr. were 2.61 and 2.68.

After the electrolysis in which the V_i value was 2.61, the anolyte was hydrolyzed with 250 ml. of 6*M* hydrochloric acid. The hydrolyzate was then extracted continuously with petroleum ether for 24 hr. Distillation of the petroleum ether left a red solid which weighed 3.0735 g. The solid was dissolved in a measured volume of petroleum ether and an aliquot containing 1.1870 g. was placed on an alumina column. Elution with chloroform–petroleum ether (1:19) gave 0.0540 g. of a red solid, m.p. 64–65°. The infrared spectrum taken in 10% chloroform solution was identical with that of a corresponding solution of authentic azobenzene.

A quantitative analysis was made of the remaining original red solid by an infrared spectrophotometric method. The spectrum of the unknown in 10% chloroform solution was compared with the spectra of known mixtures of azoxybenzene and azobenzene. It was found that the spectrum of the original red solid was identical with that of a synthetic mixture containing 5.65% azobenzene. Calculation showed that azobenzene was formed in 94.6% yield based on the oxidation of aluminum from its initial mean valence state to the tripositive state by azoxybenzene.

Electrolyses with azobenzene as additive. A number of electrolyses in each of which the anolyte contained 3.000 g. of azobenzene were carried out at an initial current of 0.012 amp. and a cell voltage of 150 V. The V_i values obtained after electrolysis for 22 hr. were 3.00, 2.67, and 2.78.

After the electrolysis in which the V_i value was 2.67, the anolyte was hydrolyzed with ice water and permitted to stand for 2 hr. The mixture was filtered (filter-aid) and the precipitate was washed with petroleum ether to remove unchanged azobenzene and then extracted with methanol. Evaporation of the methanol left 0.2737 g. of solid, m.p. 80–104°. The solid was recrystallized from methanol and there was obtained 0.1186 g. of a colorless solid, m.p. 118–119°. The infrared spectrum was taken in 10% chloroform solution and found to be identical with that of a corresponding solution of authentic hydrazobenzene. The quantity of hydrazobenzene isolated corresponds to a 68% yield based on conversion of aluminum from its initial mean valence state to the +3 state by azobenzene.

The original aqueous filtrate was extracted with ether. Evaporation of the ether left 0.1583 g. of solid. The aqueous phase was made distinctly basic with sodium hydroxide solution and again extracted with ether. Evaporation of the ether gave a small amount of brown solid which was combined with the 0.1583 g. of solid obtained above. The combined solid was washed with petroleum ether to remove any azobenzene present. To the remaining solid was added 18% hydrochloric acid solution and the mixture was filtered. After neutralization of the filtrate, 0.0586 g. of colorless solid which had precipitated was collected by filtration. Recrystallization from water gave a colorless solid, m.p. 69–72°. The infrared spectrum (in chloroform solution) corresponded to that of 4,4′-dipyridyl dihydrate.

The dipyridyl dihydrate is believed to arise at least in part by migration of the conjugate base of tetrahydro-4,4′-dipyridyl from the catholyte to the anolyte and subsequent oxidation of the base during hydrolysis. That this is plausible was shown by the following experiment. An electrolysis of a saturated lithium chloride–pyridine solution between aluminum electrodes for 20 hr. at an initial current of 0.010 amp. and a cell voltage of 130 V. was carried out. The V_t of the aluminum entering solution was 2.94. If it is assumed that some of the conjugate base of tetrahydro-4,4′-dipyridyl is formed by reduction of the solvent by lower valent aluminum anodically generated, calculation shows that only 18 mg. of dipyridyl should have been formed; actually 58 mg. was isolated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Metalation of 12H-Benzo[a]phenothiazine with *n*-Butyllithium

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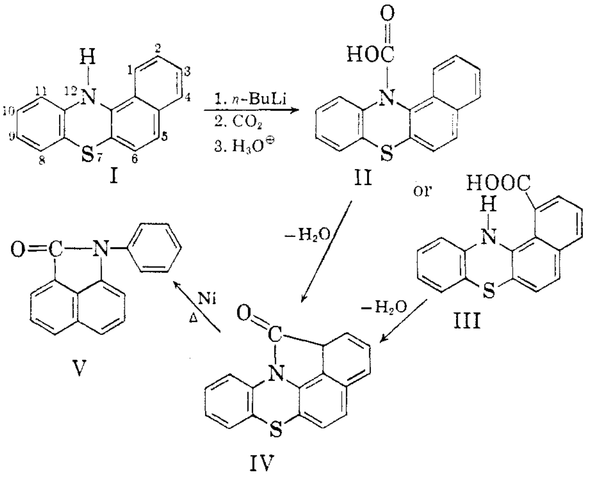
The metalation of 12H-benzo[a]phenothiazine with *n*-butyllithium followed by treatment with carbon dioxide produces 12H-benzo[a]phenothiazine-1-carboxylic acid in 94% yield. The structure of this acid is proved by its dehydration to a lactam and desulfurization to the known *N*-phenylnaphthastyril.

The metalation of a variety of heterocyclic molecules with organolithium reagents has demonstrated that this reaction is often characterized by 1) introduction of the lithium atom at positions adjacent to heteroatoms, 2) good yields, and 3) rapid reaction under mild conditions. As the positions adjacent to heteroatoms are often not the positions involved in other common substitution reactions, the metalation reaction offers a useful and convenient synthetic technique.

As a part of recent investigations[1] of the chemistry of 12H-benzo[a]phenothiazine and derivatives thereof, we have examined the metalation of this polynuclear heterocyclic type with *n*-butyllithium. Relatively few heterocyclic molecules containing >N—H bonds metalate well. The active hydrogen is rapidly replaced by metal and the resulting heterocyclic anion $>\text{N}:^-$ resists metalation. Examples of this from our work are the failures of C-metalation with pyrrole,[2] indole,[3] and imidazole,[4] although the *N*-alkyl and *N*-aryl types metalate smoothly. Carbazole[5] and pyrazole[6] metalate only in poor yield. Phenothiazine is an exception, however, as it metalates readily in 52% yield in the 1-position.[7]

Treatment of 12H-benzo[a]phenothiazine (I) with a three-fold excess of *n*-butyllithium in ether produced subsequent to carbonation a 94% yield of a deep red monocarboxylic acid derivative of I. The carboxylic acid was rather unstable and could not be purified by crystallization although it had a correct analysis and melted sharply at 136–137° with loss of water vapor. Heating the carboxylic acid above its melting point caused its conversion, by loss of a molecule of water, to a bright orange-red neutral compound. These results suggested either structure II or III for the monocarboxylic and the lactam IV for the dehydration product.



Structure II was eliminated as a possibility, as no carboxylic acid was isolated from an experiment comparable to the first metalation in which equimolar amounts of organolithium and benzophenothiazine were used.

The structure of IV was proved by its desulfurization with Raney nickel to *N*-phenylnaphthastyril (V). The latter compound was identical with a synthetic sample prepared *via* the route indicated.

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