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The Kolbe Electrolysis in Dimethylformamide

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Previous reports[1] from this laboratory have indicated the efficacy of *N*,*N*-dialkylamides in encouraging the dimerization of cathodically generated organic free radicals. This note describes an extension of the principle to anodic syntheses and presents the results of attempts to improve the yield of dimer in the Kolbe electrolysis[2] of two organic acids.

The most commonly used solvents for the Kolbe electrosynthesis are methanol and water. To a varying degree the Kolbe dimer is accompanied by ethers, alcohols, esters, and monomeric paraffins and olefins.[3] The failure to isolate higher yields of dimer in many of the reactions can be ascribed in part to diversion of the intermediate by reaction with the solvent. To obviate this difficulty a nonreacting, highly polar solvent, dimethylformamide, was used as the electrolysis medium.

The electrolysis of diphenylacetic acid in methanol has been studied previously by Riccobini[4] and by v. d. Hoek and Nauta.[5] In methanol-pyridine mixtures, these workers obtained 6% and 8.9% respectively of tetraphenylethane. Among other products, the latter workers obtained 42.6% of methyl benzhydryl ether. In our hands the electrolysis of diphenylacetic acid in methanol with triethylamine added as the base afforded an 80% yield of methyl benzhydryl ether identified by infrared comparison with authentic material. No tetraphenylethane could be isolated. Likewise, Linstead, Shephard, and Weedon[6] obtained a 73% yield of benzhydrol on saponification of the acetate formed from the electrolysis of diphenylacetic acid in acetic acid.

When the electrolysis medium was changed to dimethylformamide, a 24% yield of tetraphenylethane was obtained. This experiment was conducted for the isolation of only the Kolbe dimer and no attempt was made to find other products.

No description of the Kolbe electrolysis of hydratropic acid could be found in the literature and it was studied in somewhat more detail. Triethylamine again served as the base and the electrolysis was performed in methanol and in dimethylformamide.

In methanol the products obtained in minor amounts included styrene, α-phenethyl alcohol and acetophenone. The major products were 21% of 2,3-diphenylbutane (*meso* and *dl*) and 20% of methyl α-phenethyl ether. The products were analyzed and identified through infrared spectroscopy, vapor phase chromatography and formation of derivatives.

All of the products can be readily explained by the intermediate formation of an α-methylbenzyl radical which can dimerize, react with the solvent or with radicals generated from the solvent, be oxidized, or lose a hydrogen atom.

In dimethylformamide as the solvent the amount of dimer was doubled. 2,3-Diphenylbutane (*meso* and *dl*) was isolated in 41% yield and α-phenethyl alcohol was obtained in 8.2% yield. The latter product could arise from the reaction of the intermediary radical with water present in the dimethylformamide.

It thus appears that dimethylformamide is a good solvent in which to perform the Kolbe electrosynthesis to the relative exclusion of the common side products.

EXPERIMENTAL

All melting points and boiling points are uncorrected. A Perkin-Elmer *154B* vapor fractometer with a "K" column and helium as the carrier gas was used for analysis.

Electrolysis procedure. The electrolysis cell consisted of a 150 ml. tall-form beaker containing the appropriate solution. The cell was cooled with an ice water bath and the cell contents were mixed with a magnetic stirrer. The electrodes were pieces of smooth platinum, 2 cm. × 3 cm., 1 cm. apart and totally immersed in the solution. Current was supplied by a voltage regulated D.C. power supply. An ammeter was connected in series. The initial and final applied voltages for each experiment are indicated. The current was 0.4 amp. and did not vary more than 10% during any of the electrolyses. In each case a solution of 0.1 mol. of the acid, 3 ml. of triethylamine, and 100 ml. of the solvent was used.

Electrolyses. Diphenylacetic acid in methanol. The solution was electrolyzed for 20 hr. and the voltage was increased from 95 volts to 135 volts during the electrolysis. The methanol was partially evaporated at room temperature and the dark residue was poured into a liter of salt water and extracted four times with chloroform. The extract was washed twice with saturated sodium bicarbonate solution and several times with water. It was dried over magnesium sulfate and the chloroform was distilled, leaving a dark tar which would not crystallize. Distillation at 3 mm. gave 16 g. (80%) of methyl benzhydryl ether. Redistillation afforded 15 g., b.p. 86–90° at 0.3 mm., n_D^{28} 1.5623 (reported[7]

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n_D^{20} 1.5685). The infrared spectrum of an authentic sample was identical with that of the electrolysis product.

Diphenylacetic acid in dimethylformamide. The solution was electrolyzed for 17.8 hr. and the voltage was increased from 130 volts to 220 volts during the electrolysis. The reaction mixture was poured into water and extracted three times with ether. Some organic material remained suspended in the ether layer and it was filtered, air dried, and crystallized from chloroform. The ether extract was washed with water, sodium bicarbonate solution, and again with water. The ether was distilled *in vacuo* and the residue was crystallized from chloroform. A further crop of crystals was obtained on concentration of the combined chloroform mother liquors.

A total of 4 g. (24%) of crude product was obtained and was recrystallized from chloroform, m.p. 207–208°. A mixed m.p. with authentic tetraphenylethane[8] was undepressed at 206–207°.

Hydratropic acid[9] *in methanol.* The solution was electrolyzed for 10.7 hr. and the voltage was increased from 80 volts to 120 volts during the electrolysis. The reaction mixture was poured into a liter of salt water and was extracted three times with ether. The ether was washed successively with water, saturated sodium bicarbonate solution, water, 1:1 hydrochloric acid, water, sodium bicarbonate solution, and again with water. After drying over magnesium sulfate the ether was distilled through a Vigreux column and the yellowish residue was distilled at 19 mm. A clear liquid, 3.1 g., b.p. 56–60°, n_D^{28} 1.4950 (reported[10] for methyl α-phenethyl ether n_D^{25} 1.4911) was obtained as the first fraction. Analysis by vapor phase chromatography showed it to consist of 87% of α-phenethyl methyl ether, 3% of styrene (dibromide, m.p. 70–71°, reported[11] m.p. 73°) and a third unidentified component.

The residue was a tan oil, 5.9 g., which solidified on cooling. Crystallization from methanol afforded 721 mg. (6.9%) of solid, m.p. 122–123°, mixed m.p. with authentic *meso*-2,3-diphenylbutane, 122–123°.

The methanol mother liquor was distilled at 0.08 mm. through a short path still. Two fractions were collected: (1) 2.262 g., n_D^{28} 1.5408 and (2) 1.042 g., n_D^{28} 1.5523. Analysis by vapor phase chromatography indicated the following total yield: *meso* and DL-2,3-diphenylbutane, 2.2 g. (21%); α-phenethyl methyl ether, 2.7 g. (19.9%); α-phenethyl alcohol, 0.18 g. (1.5%); and acetophenone, traces.

The infrared spectra of fractions (1) and (2) confirm the presence of the identified substances. A pair of bands at 5.88μ and 7.96μ seem to indicate that the unisolated and unidentified substance retained by the column is an ester.

Hydratropic acid in dimethylformamide. The solution was electrolyzed for 10.3 hr. and the voltage was increased from 130 volts to 260 volts during the electrolysis. The reaction mixture was poured into a liter of salt water and extracted four times with 150-ml. portions of ether. The ether extract was washed successively with water, 1:1 hydrochloric acid, water, saturated sodium bicarbonate solution, again with water, and dried over magnesium sulfate. The ether was distilled through a Vigreux column and the residue was taken up in methanol. Cooling afforded 1.32 g. of *meso*-2,3-diphenylbutane, m.p. 116–120°. The methanol mother liquor was distilled *in vacuo* and three fractions were obtained: (1) 0.7 g., b.p. 96–112° at 15 mm., n_D^{25} 1.5170; (2) 0.4 g., b.p. 112–145° at 15 mm., n_D^{25} 1.5238; (3) 2.8 g., b.p. 115–145° at 0.8 mm., n_D^{25} 1.5455; a further 0.1 g. of *meso*-2,3-diphenylbutane was obtained as a solid in the distillation apparatus. Fractions (1), (2), and (3) were analyzed by vapor phase chromatography.

The total yield of *meso* and *dl*-2,3-diphenylbutane was 4.3 g. (41%) and of α-phenethyl alcohol, 1 g. (8.2%).

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Palladium Catalysts. IX.[1] Kinetic Studies

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Previous papers report that the qualitative character of palladium-on-carbon catalysts may be influenced by such factors as the presence of other metals,[4] the ratio of metal to carrier,[5] and by the nature of the anion present when the metal is deposited on the carrier.[1,6] There is also evidence that a product formed during the hydrogenation reaction may inhibit the catalytic reaction.[7] Results of further studies along these lines are now presented.

In order to control external variables during the hydrogenation reaction the apparatus shown schematically in Fig. 1 was designed. With it one may maintain a constant pressure of hydrogen within the vicinity of one atmosphere throughout the entire course of the reaction; the rate of agitation is constant; the temperature may be controlled to within 0.2°. Results obtained with this apparatus permit the observation of the kinetic order of the reaction and allow for more valid comparison of one reaction with another and, it is hoped, contribute to a better understanding of the catalytic mechanisms.

In Fig. 2 are shown graphically the effects of temperature variation on the reduction of nitrobenzene. In all instances the rate of hydrogen absorption with respect to substrate is zero order as was previously observed by Rampino and Nord.[8]

The phenylcarbonyl compounds with one molecule of hydrogen form the corresponding carbinols, and with two molecules of hydrogen undergo

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