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Syntheses by Free-radical Reactions. X. Electrochemical Additive Dimerizations

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Radicals produced by the discharge of carboxylate anions at an anode have been shown to attack 1,3-dienes to give butenyl radicals which dimerize or react with other radical species present at the anode. These reactions have been employed in the preparation of olefins, dienes and esters of unsaturated dicarboxylic acids.

Aliphatic free radicals formed by attack of hydroxyl radicals on saturated aliphatic compounds have been shown to add to 1,3-dienes to give resonance-stabilized butenyl radicals which dimerize to produce straight- and branched-chain products arising by 1,4- and 1,2-incorporation of the diene. This process, which has been termed additive dimerization,[1] may be represented by reactions (1) and (2) in which R· is the aliphatic free radical and M is the diene.

$$R\cdot + M \longrightarrow R{-}M\cdot \qquad (1)$$

$$2R{-}M\cdot \longrightarrow R{-}M{-}M{-}R \qquad (2)$$

We have found that additive dimerization also occurs when carboxylates are electrolyzed in the presence of 1,3-dienes. These electrochemical additive dimerizations are analogous to the formation of 3,4-diphenylhexane and 4,5-diphenyloctane by electrolysis of mixtures of styrene with sodium acetate and with sodium propionate in the respective anhydrous acids as solvents.[2]

According to the generally accepted free-radical mechanism,[3] the Kolbe reaction proceeds by discharge of anions to give acyloxy radicals that undergo a secondary reaction to form aliphatic free radicals and carbon dioxide. When this reaction is

$$RCOO^- \overset{-e}{\rightleftharpoons} RCOO\cdot \qquad (3)$$

$$RCOO\cdot \longrightarrow R\cdot + CO_2 \qquad (4)$$

conducted in the presence of a 1,3-diene, additive dimers are formed in accordance with reactions 1 and 2. Other products include those of the normal Kolbe synthesis (5) and those formed by reaction 6.

$$2R\cdot \longrightarrow R{-}R \qquad (5)$$

$$R\cdot + R{-}M\cdot \longrightarrow R{-}M{-}R \qquad (6)$$

The formation of products of the types R–R and R–M–R was not observed in additive dimerizations initiated with hydroxyl radicals.[2] Apparently a higher ratio of alkyl radicals to butenyl radicals is obtained at the electrode surface than in systems where the alkyl radicals are produced by reaction with hydroxyl radicals. This may be due to the difficulty of maintaining a high concentration of diene in the vicinity of the electrode.

In general, electrochemical additive dimerizations are brought about by electrolyzing a solution of a diene, a carboxylic acid, and an alkali salt of the carboxylic acid in a suitable solvent. Methanol solutions of these components were homogeneous and were sufficiently good conductors. Additive dimers were not formed in aqueous emulsions of butadiene. The electrolyses were carried out at temperatures of about 0 to −15° to maintain sufficient concentrations of diene in the solutions. 1,3-Butadiene was used as the diene component in most of the reactions studied. Isoprene reacted in a similar manner and has been used in a few electrolyses.

Electrolysis of methanol solutions of acetic acid, potassium acetate, and butadiene gave 11–26% yields of 3-hexene and 12–58% C_{10}-dienes. The major part of the C_{10}-product was 3,7-decadiene, formed from methyl radicals and 1,4-incorporation of two butadiene units. Smaller amounts of isomeric branched-chain C_{10}-dienes, presumably formed by 1,2-addition and mixed 1,4- and 1,2-additions, also were obtained. During these reactions, considerable amounts of gas were evolved. Since the products isolated accounted for only 30–50% of the methyl radicals which should have been formed, based on current consumed, it is assumed that the gaseous product was ethane.

When butadiene was replaced by isoprene in this reaction, 3-methyl-3-hexene and higher hydrocarbons, presumably additive dimers, were obtained. The electrolysis of trifluoroacetic acid in the presence of butadiene resulted in a variety of products, of which only the C_{10}-straight-chain additive dimer, 1,1,1,10,10,10-hexafluoro-3,7-decadiene, was identified.

Derivatives of dicarboxylic acids also have been employed in these syntheses. Of particular interest is the use of potassium ethyl oxalate as a novel source of carbethoxy radicals. Electrolysis of the oxalate has been reported to give ethylene and carbon dioxide.[4] However, when the electrolysis was conducted in the presence of butadiene, the carbethoxy radicals were sufficiently long-lived to react with the diene. About 40% of the product was an unsaturated ester which was hydrogenated and then saponified to obtain sebacic acid. Accordingly, the electrolysis product is the straight-chain additive dimer, diethyl 3,7-decadiene-1,10-dioate.[5]

Similarly, α,β-unsaturated acids[6] and monoesters of unsaturated dibasic acids such as fumaric acid[7] do not undergo anodic coupling in the Kolbe reaction. However, electrolysis of a solution containing potassium ethyl maleate and butadiene gave a small amount of an unsaturated diester which was hydrogenated and then saponified to sebacic

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[1] D. D. Coffman and E. L. Jenner, THIS JOURNAL, **80**, 2872 (1958).

[2] S. Goldschmidt and E. Stöckl, *Chem. Ber.*, **85**, 630 (1952).

[3] See B. C. L. Weedon, *Quart. Revs.*, **6**, 380 (1952), for a discussion of the mechanism of the Kolbe reaction.

[4] A. Crum-Brown and G. Walker, *Ann.*, **274**, 71 (1893).

[5] R. V. Lindsey, Jr., and M. L. Peterson, U. S. Patent 2,680,713 (1954).

[6] J. Peterson, *Z. Elektrochem.*, **18**, 711 (1912).

[7] P. Karrer and M. Stoll, *Helv. Chim. Acta*, **14**, 1189 (1931).

acid. The product apparently arises from combination of two substituted vinyl radicals, $\cdot CH{=}CHCOOC_2H_5$, with one butadiene unit. This same radical may have participated in the formation of a product believed to have the structure $C_2H_5OOCCH{=}CHCOOCH{=}CHCOOC_2H_5$ that was obtained during the electrolysis of ethyl hydrogen maleate in the presence of sodium acetate.[7]

When monoester salts of malonic, succinic and adipic acid were electrolyzed with butadiene, esters of straight- and branched-chain, unsaturated dicarboxylic acids were obtained. These straight-chain additive dimers were catalytically hydrogenated and then saponified to obtain dodecanedioic, tetradecanedioic and octadecanedioic acids, respectively.[5]

Experimental

Electrolytic Cell.—Electrolyses were carried out in a closed vessel fitted with a condenser cooled with solid carbon dioxide and acetone, and two platinum electrodes having an area of 55 cm.^{2} on each face and spaced about 2.5 cm. apart. A carbon anode was used successfully in several electrolyses. The choice of materials for the cathode was not critical. The anode and cathode were not separated by a diaphragm because no reduction of the products was observed at the cathode. Current was provided by storage batteries connected in series. A switching device permitted variation of the applied voltage in 2-volt increments. Sufficient voltage was applied to obtain a practical current and rate of reaction. Since the solutions used in most of this work had high resistances, much heat was generated. Accordingly, the electrolytic cell was cooled externally in a bath of solid carbon dioxide and acetone. These reactions gave mixtures of products that were usually difficult to separate, and experimental procedures were designed mainly to establish the formation of linear additive dimers. For this reason, no attempt has been made to calculate current efficiencies or chemical yields.

Electrolysis of Acetic Acid.—A homogeneous solution of 300 ml. of methanol, 40 g. of acetic acid, 50 g. of potassium acetate and 150 g. of 1,3-butadiene was electrolyzed at 5° with an applied potential of about 30 v. for 625 min. at an average current of 1.5 amp. until the reaction mixture became slightly alkaline, at which point 0.6 faraday had been passed through the cell. The electrolyzed solution was added to 1 l. of cold water, and the hydrocarbon layer which separated was dried and distilled to obtain 3.4 g. of 3-hexene, b.p. 63–64°, $n^{25}\mathrm{D}$ 1.3905 (lit.[8] b.p. 64°, $n^{19}\mathrm{D}$ 1.394), and 6.2 g. of hydrocarbons boiling at 153–163°. Redistillation of the latter material gave two fractions: I, b.p. 153–156°, $n^{26}\mathrm{D}$ 1.4333, and II, b.p. 162–164°, $n^{26}\mathrm{D}$ 1.4355.

The physical constants of II agreed with those of 3,7-decadiene, b.p. 166.5°, $n^{23}\mathrm{D}$ 1.4356.[9] A methanol solution of fraction II was ozonized, hydrogenated with palladium-on-charcoal catalyst, and distilled. Addition of 2,4-dinitrophenylhydrazine to the distillate gave propionaldehyde 2,4-dinitrophenylhydrazone, m.p. 139–142°, undepressed on admixture with an authentic sample.

Fraction I is believed to be a mixture of branched-chain isomeric decadienes formed by 1,2- and mixed 1,2- and 1,4-additions of the diene. Ozonization and treatment as described above gave a mixture of 2,4-dinitrophenylhydrazones which melted over a wide range. By chromatographing the mixture on an alumina column, propionaldehyde 2,4-dinitrophenylhydrazone was isolated.

A similar electrolysis conducted at 10° with isoprene in place of butadiene gave two corresponding fractions, b.p. 92–97° and 109–119° (43 mm.). No attempt was made to characterize the higher-boiling fraction because of the large number of possible isomers. By analogy to the results obtained with butadiene, the lower-boiling product was assumed to be 3-methyl-3-hexene (lit.[10] b.p. 94°).

Electrolysis of Trifluoroacetic Acid.—A mixture of 300 ml. of methanol, 50 g. of trifluoroacetic acid, 4 g. of potassium hydroxide and 150 ml. of butadiene was electrolyzed at −10° at an applied potential of about 17 v. for 395 min. with an average current of 4.0 amp., or until 1.0 faraday had been passed through the cell, at which point the solution was basic. Water (500 ml.) was added, the hydrocarbon layer was separated, and the aqueous phase was extracted twice with *n*-pentane. Distillation of the combined hydrocarbon layer and extracts gave 34.7 g. of a mixture of products which boiled over the range 35–170°. Distillation through a micro spinning-band column did not produce any sharp cuts. A fraction boiling at 168–170° was examined.

Anal. Calcd. for $C_{10}H_{12}F_6$: C, 48.7; H, 4.92. Found: C, 48.2; H, 5.47.

Ozonization, hydrogenation and reaction with 2,4-dinitrophenylhydrazine as previously described gave the 2,4-dinitrophenylhydrazone of 3,3,3-trifluoropropionaldehyde, m.p. 146–149° (lit.[11] 150.2–150.8°).

Electrolysis of Ethyl Hydrogen Oxalate.—A solution of 350 ml. of methanol, 10 g. of potassium ethyl oxalate, 40 g. of ethyl hydrogen oxalate and 150 ml. of butadiene was electrolyzed at about −15° for 360 min. at an average current of 3.0 amp. until 0.67 faraday had been passed through the cell. The applied potential was gradually increased from 36 to 60 v. At the end of the electrolysis, the solution showed a slightly basic reaction to *p*H paper. The solution was reduced to a volume of 50 ml., 100 ml. of water was added, and the mixture was extracted with ether. The extracts were dried over magnesium sulfate and distilled to obtain 6 g. of lower boiling material, 6 g. boiling at 137–145° (4 mm.) and 7.4 g. boiling at 148–151° (4 mm.). A methanol solution of 6.0 g. of the fraction that distilled at 148–151° (4 mm.) was hydrogenated over a palladium-on-charcoal catalyst and then saponified in an aqueous ethanol solution of sodium hydroxide. Acidification gave 4.0 g. of a solid which, after crystallization from ethyl acetate, melted at 132–134°, undepressed on admixture with sebacic acid.

Electrolysis of Ethyl Hydrogen Maleate.—The electrolysis of methanol solutions of ethyl hydrogen maleate and either butadiene or isoprene formed films on the anode which greatly reduced the conductance of the electrolytic cell. Films were not formed in the absence of diene. A solution of 350 ml. of methanol, 50 ml. of water, 100 ml. of butadiene, 35.6 g. of ethyl hydrogen maleate and 14 g. of potassium ethyl maleate was electrolyzed at −10° with an applied potential of 88 v. for 840 min. at an average current of 1 amp., or until about 0.5 faraday had been passed through the cell. Work-up of the products as previously described gave 14.4 g. of a mixture of products boiling over the range 64–119° (3 mm.). A fraction (4.3 g.), b.p. 115–119° (3 mm.), was hydrogenated in methanol over a palladium-on-charcoal catalyst and then saponified to obtain sebacic acid, m.p. 132–134°, undepressed on admixture with an authentic sample.

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[8] P. L. R. Lespieau and J. G. Wiemann, *Bull. soc. chim.*, **45**, 627 (1929).

[9] Ch. Prevost and G. Richard, *ibid.*, **49**, 1368 (1931).

[10] A. Favorskii and J. Zalersskii-Kibardine, *C. A.*, **20**, 2481 (1926).

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