44. *Electrolytic Reduction of Organic Compounds. Part I. Analogies between Cathodic Reduction and the Action of Dissolving Metals. Reduction of Sorbic Acid.*

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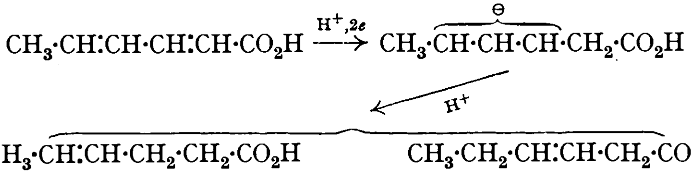
BURTON and INGOLD (J., 1929, 2022) have suggested a theory to explain the process of reduction of an olefinic double bond by metals dissolving in suitable media. The scheme involves the successive addition to the unsaturated system of a proton together with two electrons supplied by the dissolving metal, and a second proton. The theory explains the susceptibility of Δ^{α}-unsaturated acids or ketones to attack by this type of reducing agent and enables the principles of prototropy to be applied in order to predict the orienting effects of substituents in the reduction of certain butadiene acids.

Illustrating their case by sorbic acid (I), Burton and Ingold argued that the second proton would be preferentially attached at that point in the ion (II) at which the electron density was the higher. Since by this theory the ratio of the amounts of the two dihydro-compounds is essentially determined by structure, it should be independent of the reducing system employed. These authors stated that they had intended to investigate quantitatively the reduction of sorbic acid by a variety of dissolving metals, the object being to vary the ease of access of electrons to the organic molecule. This project was, however, frustrated by experimental difficulties and satisfactory results were obtained with only sodium and aluminium amalgams.

(I.)

(II.)

$$CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H \xrightarrow{H^+,2e} CH_3{\cdot}\overbrace{CH{\cdot}CH{\cdot}CH}^{\ominus}{\cdot}CH_2{\cdot}CO_2H \xrightarrow{H^+} \overbrace{CH_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H \qquad CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H}$$

Although we also have not been able to extend Burton and Ingold's experiments in this direction, we have investigated the electrolytic reduction of sorbic acid and of the sorbate ion at a variety of metallic cathodes. We have shown that the hexenoic acids produced consist only of the Δ^{β}- and the Δ^{γ}-isomeride in relative amounts which are in each case characteristic of the unsaturated entity to within the range and accuracy of our experiments. This ratio, moreover, as will be evident from the table, is substantially equal to that which has been obtained in reductions by aluminium and sodium amalgams.

Δ^{γ}-Hexenoic Acid (%) in " Hydrosorbic " Acid.

	Medium : Aqueous			
Reducing agent.	NaOH.	$NaHCO_3$.	$CH_3{\cdot}CO_2H$.	H_2SO_4.
Hg cathode	40	41	54	52
Cd ,,	39	—	54	—
Cu ,,	40	—	50	—
NaHg *	—	40	55	—
AlHg *	45	45	—	—

* Burton and Ingold, *loc. cit.*; cf. Evans and Farmer, J., 1928, 1644; Goldberg and Linstead, *ibid.*, p. 2343.

This result is immediately intelligible in the case of the mercury cathode at least, if it is assumed that the electrical conditions obtaining at the cathode when evolving hydrogen are the same as those at the mercury surface of dilute sodium amalgam in the same medium, the sodium furnishing by its solution pressure the necessary cathodic potential. Such a view implies that all reactive amalgams should behave similarly, and excludes the idea of the intermediate addition of sodium or other metal atoms to the double bond (cf. Willstätter, Seitz, and Bumm, *Ber.*, 1928, **61**, 871). In support of this contention we have shown that anthracene can be reduced to the 9 : 10-dihydro-compound by sodium, aluminium, and magnesium amalgams and also at a mercury cathode in an alcoholic solution of sodium hydroxide, ammonium sulphate and ammonia, and tetramethylammonium hydroxide : one can hardly suppose that all these metals and quasi-metals like ammonium are added to the hydrocarbon.

The results for sorbic acid suggest an equivalence in mechanism between reduction by the reagents considered by Burton and Ingold and reduction at cathodes, a conclusion which is supported by many recorded observations. Comment has been passed on the similarities between the action of a mercury or lead cathode and dilute sodium amalgam in the reduction of Δ^{α}-double bonds (Marie, *Compt. rend.*, 1903, **186**, 1331; " Organic Syntheses," 1929, **9**, 42; Law, J., 1912, **101**, 1016); and between a lead cathode and sodium-lead alloy in the reduction of many substituted acetoacetic esters and quaternary ammonium salts (Fichter and Stenzl, *Helv. Chim. Acta*, 1933, **16**, 571; 1934, **17**, 669). We would stress also the great similarity of the behaviour of lead and mercury cathodes, and of dissolving metals and amalgams in the nuclear and the side-chain reduction of aromatic acids and esters (Aschan, *Ber.*, 1891, **24**, 1864; Weil, *Ber.*, 1908, **41**, 4147; Tafel and Friedrichs, *Ber.*, 1904, **37**, 3187; Mettler, *Ber.*, 1905, **38**, 1745 *et seq.*). Even more striking is the electrolytic analogue of Clemmensen's method of reduction : the carbonyl group may successfully be reduced to a methylene group in strongly acid solutions at cathodes of cadmium, lead, mercury and even amalgamated zinc (Schepss, *Ber.*, 1913, **46**, 2564; Swann and Feldmann, *Trans. Amer. Electrochem. Soc.*, 1935, **67**, 195; Shima, *Mem. Coll. Sci. Kyoto*, 1929, *A*, **12**, 73).

Although the practical value of the electrolytic method is limited to reductions involving a fairly highly conducting catholyte, the process, nevertheless, has the advantage of permitting the employment of many different metallic cathodes, of which one may be much more efficient than another. Mercury, for instance, either as cathode or as amalgam, reduces sorbic acid to mixtures which always contain considerable proportions of pinacol-like " bimolecular " compounds. This behaviour appears to be a peculiarity of mercury, since copper and cadmium, which of course cannot be employed as dissolving metals, produce, as cathodes, smooth dihydrogenation of this acid.

In our experiments very little reduction was observed at a tin cathode and none at lead, smooth nickel, and shiny platinum. We were careful to bear in mind Tafel's injunctions (*Ber.*, 1900, **33**, 2209) concerning the adverse influence of impurities on the reducing efficiency of a lead cathode; our sample (purchased from A. Hilger, Ltd.) was guaranteed to contain less than 0·001% of foreign metals, and in spite of that it failed completely.

It has been suggested (cf. Brockman, " Electro-organic Chemistry," 1926, p. 275) that the magnitude of the hydrogen overvoltage of a cathode is an important factor in the electrolytic reduction of Δ^{α}-double bonds. This idea does not agree with our experiments, which indicate a reducing efficiency according to the series Cu, Hg $>$ Cd $\gg$ Sn $>$ Pt, Ni (smooth). On the other hand, hydrogen overvoltage seems important for the reduction of aliphatic and aromatic aldehydes and aliphatic ketones to hydrocarbons (cf. the above remarks on the Clemmensen reduction and its electrolytic counterpart).

The remarks made by Ingold and Rogers (J., 1935, 719) when discussing the peculiarities of amalgams in reduction may satisfactorily be extended to electrolytic reductions of the type considered in this paper. The activated stage in reduction is an electron transfer, governed by an interfacial potential barrier of the kind considered in the theory of hydrogen overvoltage (Gurney, *Proc. Roy. Soc.*, 1931, [*A*], **134**, 137). Efficiency in reduction implies that the electrons encounter less resistance due to the barrier between the cathode and the organic molecule than to that between the cathode and the solvent. A high hydrogen overvoltage, which implies a large cathode-solvent barrier, will permit the cathode to acquire a high negative potential, and will therefore facilitate the adsorption of the organic molecule by means of its reducible positive centres.

EXPERIMENTAL.

Preparation of Materials.—Sorbic acid, obtained in quantity by the condensation of malonic acid and freshly distilled crotonaldehyde in dry pyridine (Döbner, *Ber.*, 1900, **33**, 2140), had m. p. 134° (from petroleum, b. p. 80—100°).

Δ^{α}-*n*-Hexenoic acid made by Goldberg and Linstead's method (J., 1928, 2351) and recrystallised from petroleum (b. p. 40—60°) had m. p. 32·2°. The anilide prepared from the chloride had m. p. 110° (G. and L., *loc. cit.*, give 110°) (Found : C, 76·0; H, 8·0; N, 7·8. Calc. : C, 76·1; H, 8·0; N, 7·4%).

Δ^{β}-*n*-Hexenoic acid (cf. Linstead, Noble, and Boorman, J., 1933, 557) had b. p. 116—117°/18 mm. and m. p. 11°; these authors give m. p. 12°. The anilide had m. p. 55° (Found : C, 76·4; H, 8·0; N, 7·6. Calc. : C, 76·1; H, 8·0; N, 7·4%).

Δ^{γ}-*n*-Hexenoic acid, prepared in 20% yield by Letch and Linstead's method (J., 1934, 1994) from " hydrosorbic " acid obtained by the reduction of sorbic acid at a spongy copper cathode in alkaline solution (see expt. 9), had b. p. 109—110°/18 mm. and m. p. 1° (L. and L., *loc. cit.*, give m. p. 1°). The anilide had m. p. 87° (Found : C, 76·1; H, 8·1; N, 7·5. Calc. : C, 76·1; H, 8·0; N, 7·4%).

Reduction Technique.—Exploratory experiments were carried out in what we have called a differential apparatus (cf. Pomilio, *Z. Elektrochem.*, 1915, **21**, 444). Briefly, two similar electrolysis cells, embodying porous pots (7 × 2 cm. in diameter), were connected in series, the pots forming the cathode compartments. One cell served as a hydrogen coulombmeter, the other as a reduction cell. The hydrogen evolution from each unit was measured in two similar 5 c.c. gas burettes, immersed, up to their zero marks, in water. The reducing efficiency of any cathode in a given medium could, in this way, be rapidly determined with the use of a very small amount of material (0·1 g.). The current was 0·14 amp.

Reductions on a large scale (involving 10—20 g. of sorbic acid) were carried out in tall beakers (1000 c.c.); the cylindrical porous pots forming the anode compartments measured 16 × 4 cm.

in diameter and were conditioned before use as directed by Tafel (*Ber.*, 1900, **33**, 2216). Where possible, cylindrical cathodes (15 × 7 cm. in diameter) were used with strips of platinum foil as anodes, the anolyte was the same medium as the catholyte with the addition of a suitable salt (sodium acetate, sulphate, or carbonate) to prevent undue osmosis. A current of 1·0 amp. was used throughout and the temperature remained between 20° and 25° or was maintained within these limits by water-cooled glass spirals.

Preparation of Cathodes.—Mercury, purified by dilute nitric acid and distilled in a vacuum before use, formed, as a cathode, a layer (50 sq. cm.) a few mm. deep on the bottom of the beaker, the porous pot being suspended.

Cadmium (a commercial sample—Messrs. Harrington Bros., Ltd.) was fashioned into a cylinder and cleaned with dilute nitric acid. The reducing properties of the cathode were not influenced by electro-deposition of a spongy layer of cadmium.

Tin. A specimen of commercial sheet tin was used (Messrs. Johnson and Matthey and Co., Ltd.).

Lead. Two specimens were available: (a) a sample of assay lead (Messrs. Hopkin and Williams, Ltd.) which was shown by spectrographic analysis to contain the following impurities: Bi, 0·04—0·08; Cu, *ca.* 0·0002; Ag, 0·0005—0·001; Cd, 0·0002%; Tl, trace; and (b) a specimen of spectrographically pure lead (Messrs. Adam Hilger, Ltd.) which was guaranteed to contain less than 0·001% of impurity (probably Bi). The electrodes were alternately electrolytically oxidised and reduced in 2*N*-sulphuric acid and were preserved in the oxidised condition under distilled water (cf. Tafel, *loc. cit.*).

Copper, in the form of gauze (30 mesh), was first oxidised in air and then covered with a substantial deposit of copper by electrolysis of an acid solution of pure copper sulphate. The electrode was used immediately after washing.

Isolation and Purification of Reduction Products.—(a) *Reduction in aqueous acetic acid.* Acetic acid purified by Orton and Bradfield's method (J., 1927, 983), diluted to 70%, and made 0·5*M* with respect to sodium acetate, was employed as catholyte. On completion of a reduction the liquid (500—600 c.c.) was filtered, treated with 700 c.c. of concentrated hydrochloric acid, and cooled below 0°. In this way the major portion of any unreduced sorbic acid was removed (cf. Burton and Ingold, *loc. cit.*). The filtrate, diluted with water (500 c.c.), was repeatedly extracted with ether (12—15 times), the extract (3—4 l.) distilled through a long column, and the acetic acid removed by fractionation in a vacuum from a Claisen flask embodying a 12" Vigreux column. By cooling a solution of the residue in petroleum (b. p. 40—60°) to − 5°, more sorbic acid could be removed. The dihydro-acids were then distilled from a small fractionating Claisen flask at a rate not exceeding 2—5 drops/min. Under these conditions any residual sorbic acid remained in the flask (cf. Burton and Ingold, *loc. cit.*). The product was again distilled before analysis. In all these experiments the yield of pure reduction product was about 86% of the theoretical, the greater part of the loss occurring during the separation of the acetic acid. High-boiling " pinacol " product, formed only at a mercury cathode, was distilled under a fraction of a mm. without decomposition.

(b) *Reduction in* 2N-*sulphuric acid.* Only one reduction was attempted, because sorbic acid was only sparingly soluble in the aqueous acid. Reduction was finally complete, the product floating on the surface of the catholyte. After thorough extraction with ether, the extract was dried over sodium sulphate and treated as in (a) with the appropriate modifications. The yield of pure reduction product was 86% (expt. 2).

(c) *Reduction in neutral and in alkaline solutions.* For reduction in neutral solution the sorbic acid was dissolved in *N*/2-sodium bicarbonate, and the solution saturated with carbon dioxide throughout the reduction; in alkaline medium, sodium sorbate dissolved in *N*-sodium hydroxide was used. In both cases, after acidification with hydrochloric acid, the procedure was as in (a), the distillation with the object of separating acetic acid being of course omitted. The yield of purified reduction product was about 94% of the theoretical.

Analysis of Reduction Products.—(a) *Addition of bromine to the hexenoic acids.* In pure glacial acetic acid solution at room temperature, the reaction between bromine and pure Δ^{α}-*n*-hexenoic acid, in initial concentrations *N*/20 and *M*/80 respectively, was slow and occurred only to the extent of about 10% in 5 hours. In 50% aqueous acetic acid as solvent, addition was rapid and quantitatively complete in 4 hours; Δ^{β}- and Δ^{γ}-*n*-hexenoic acids reacted completely in less than 2 hours.

(b) *Addition of iodine to the hexenoic acids.* Δ^{α}-*n*-Hexenoic (*M*/80) in sodium bicarbonate solution reacted with iodine (*N*/20) at room temperature only to the extent of 1·1% in 8 hours (cf. Linstead and May, J., 1927, 2565). During the same period of time the addition to Δ^{β}- and Δ^{γ}-*n*-hexenoic acids was quantitatively complete.

The analysis of the reduction product was carried out in narrow-mouthed glass-stoppered bottles (150 c.c.). The concentrations of halogen and unsaturated acid were $N/20$ and $M/80$ (had reaction occurred completely, there would thus have been 2 equivs. of halogen). Each estimation was performed in duplicate. After a suitable period of time, potassium iodide solution (10%) was added to the reaction mixture involving bromine, and concentrated hydrochloric acid to that involving sodium bicarbonate solution, the iodine liberated being titrated with $N/10$-thiosulphate.

The bromine absorbed therefore corresponds to the total dihydro-acids (Δ^{α}-, Δ^{β}-, and Δ^{γ}-*n*-hexenoic acids) present in the reduction product and is given as a percentage (*B*). The iodine absorption, which represents Δ^{β}- and Δ^{γ}-acids, is also given (*J*%). In the experiments recorded below, the substantial equality of these two figures with 100 establishes the absence of hexoic and Δ^{α}-*n*-hexenoic acids.

Ozonolysis. The method was essentially that of Burton and Ingold (*loc. cit.*). The reduction product (2—5 g.) was treated in chloroform solution at 0° with ozonised oxygen until the solution was saturated towards bromine. An artificial mixture of Δ^{β}- and Δ^{γ}-*n*-hexenoic acids (Δ^{γ}-, 50%) gave the following results: (1) 5·000 g. gave 2·300 g. of succinic acid (Found: Δ^{γ}-*n*-hexenoic acid, 44·5%); (2) 4·750 g. gave 2·170 g. of succinic acid (Found: Δ^{γ}-*n*-hexenoic acid, 44·1%); (3) 3·985 g. gave 1·822 g. of succinic acid (Found: Δ^{γ}-*n*-hexenoic acid, 44·2%). These figures give a mean factor for the conversion of Δ^{γ}-*n*-hexenoic acid into succinic acid of 88·5%, in good agreement with that (90%) found and used by the above authors.

Details of Typical Reductions.—Expt. 1. *Mercury in acetic acid.* The current efficiency was very high. Sorbic acid (20 g.) after the passage of 20 amp. hr. (theoretical for dihydro-acid, 10 amp. hr.) gave a product distilling in two fractions: (a) 6·8 g., b. p. 105—106°/14 mm. [Found: *B*, 99·4; *J*, 99·6; $\Delta^{\beta} + \Delta^{\gamma}$, 99·4; Δ^{γ} (by ozonolysis), 53·7, 54·9%]; (b) 10·2 g. of "pinacol," b. p. 180—182°/< 1 mm. [Found: C, 64·2; H, 8·0; *M* (Rast), 231; *M* (by titration as a dicarboxylic acid), 227. Calc. for $C_{10}H_{16}(CO_2H)_2$: C, 63·7; H, 8·0%; *M*, 226].

Expt. 2. *Mercury in sulphuric acid.* The reduction product from sorbic acid (20 g.) consisted of: (a) 6·4 g., a colourless liquid, b. p. 105—106°/14 mm. [Found: *B*, 99·5; *J*, 99·6; $\Delta^{\beta} + \Delta^{\gamma}$, 99·5; Δ^{γ} (by ozonolysis), 52·1%]; (b) 11·1 g. of "pinacol," b. p. 184—186°/< 1 mm. [Found: C, 64·2; H, 8·0; *M* (Rast), 231, 242; *M* (by titration as a dicarboxylic acid), 226·8].

Expt. 3. *Mercury in neutral solution.* Sorbic acid (20 g.) gave (a) a colourless liquid (15·0 g.), b. p. 103—104°/13 mm. [Found: *B*, 99·7; *J*, 99·6; $\Delta^{\beta} + \Delta^{\gamma}$, 99·6; Δ^{γ} (by ozonolysis), 40·9, 41·5, 41·1%], and (b) a light brown "pinacol" (4·1 g.), b. p. 180—183°/< 1 mm.

Expt. 4. *Mercury in alkaline solution.* Sorbic acid (18 g.) gave (a) 11·7 g., b. p. 103—104°/13 mm. [Found: *B*, 99·7; *J*, 99·5; $\Delta^{\beta} + \Delta^{\gamma}$, 99·5; Δ^{γ} (by ozonolysis), 39·3, 40·7%], and (b) 5·0 g. of "pinacol," b. p. 178—180°/< 1 mm.

Expt. 5 (*as* 4). Sorbic acid (40 g.) gave (a) a colourless liquid (27·3 g.), b. p. 100—101°/11 mm. (Found: *B*, 99·8; *J*, 99·9; $\Delta^{\beta} + \Delta^{\gamma}$, 99·8%), and (b) "pinacol" (10·7 g.), b. p. 178—181°/< 1 mm.

Expt. 6. *Cadmium in acetic acid.* The reduction was fairly efficient. Sorbic acid (10 g.) gave, after the passage of six times the theoretical (for dihydro-acid) amount of current, (a) unchanged sorbic acid (2·4 g.) and (b) 6·0 g., b. p. 108—109°/15—16 mm. [Found: *B*, 100·0; *J*, 99·7; $\Delta^{\beta} + \Delta^{\gamma}$, 99·7; Δ^{γ} (by ozonolysis), 54·0, 53·9%].

Expt. 7. *Cadmium in alkaline solution.* The reduction was more efficient than in expt. 6. Sorbic acid (20 g.) gave, after the passage of five times the theoretical (for dihydro-acid) amount of current, an acid, b. p. 100—101°/11 mm. (18·9 g.; 95%) [Found: *B*, 99·8; *J*, 99·8; $\Delta^{\beta} + \Delta^{\gamma}$, 99·8; Δ^{γ} (by ozonolysis), 38·4, 38·8%].

Expt. 8. *Copper in acetic acid.* The products from sorbic acid (12 g.) and six times the theoretical (for dihydro-acid) amount of current were: (a) unchanged sorbic acid (3·0 g.) and (b) a colourless liquid (8·0 g.), b. p. 102—103°/12 mm. [Found: *B*, 99·6; *J*, 99·3; $\Delta^{\beta} + \Delta^{\gamma}$, 99·3; Δ^{γ} (by ozonolysis), 50·0%].

Expt. 9. *Copper in alkaline solution.* Sorbic acid (20 g.) gave a 96% yield of a liquid, b. p. 102—103°/12 mm. (18·5 g.) [Found: *B*, 99·6; *J*, 99·7; $\Delta^{\beta} + \Delta^{\gamma}$, 99·6; Δ^{γ} (by ozonolysis), 39·8, 39·4%]. The current efficiency was very high.

Reduction of Anthracene.—Anthracene, dissolved in moist ethyl alcohol or, better, in dioxan, was easily reduced by magnesium or aluminium amalgam to 9 : 10-dihydroanthracene, identified by m. p. and mixed m. p. with an authentic specimen. The reduction of anthracene in ethyl-alcoholic solution by sodium amalgam has been already described (Graebe and Liebermann, *Annalen*, Suppl., 1870, **7**, 265).

Anthracene (0·1 g.) in ethyl alcohol (40 c.c., 95%) containing ammonium sulphate (0·2 g.) and aqueous ammonia (0·5 c.c.) was reduced to the dihydro-compound at a mercury cathode. No reduction occurred when the solution was acidified with sulphuric acid containing sodium sulphate. Reduction at a mercury cathode was also found to be possible in aqueous-alcoholic sodium hydroxide and tetramethylammonium hydroxide (the latter was prepared by shaking the pure chloride with silver oxide).

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