214. *The Modes of Addition to Conjugated Unsaturated Systems. Part V. The Hydrogenation of Ethyl Muconate and Sorbic and β-Vinylacrylic Acids in the Presence of Platinum.*

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FOR a number of years following Paal's investigation of the catalytic reduction of butadiene derivatives (*Ber.*, 1912, **45**, 2221) the impression had been general that the reaction between these substances and hydrogen in the presence of dispersed platinum or palladium was incapable of being arrested at the stage corresponding to the formation of dihydro-addition products (compare Vavon and Jakes, *Bull. Soc. chim.*, 1927, **41**, 81).

The first suggestion to the contrary arose in the work of Lebedev and Yakubchik (J., 1928, 823, 2190; 1929, 220), who, employing platinum as catalyst, studied the reaction of butadiene, piperylene, isoprene, βγ-dimethylbutadiene, and piperic acid, and in each case claimed the formation of mixtures containing considerable proportions of all the various possible dihydro-compounds. No analytical evidence was adduced in support of this conclusion, which was based only on a doubtful interpretation of the curves for the rate of absorption of hydrogen.

This was the situation when the present work was commenced, but during its progress two further communications have appeared; both describe the application of analytical methods to the problem, and both record the formation of dihydro-derivatives. Muskat and Knapp (*Ber.*, 1931, **64**, 779) examined the reduction, catalysed by platinum, of α-phenyl-butadiene and β-vinylacrylic acid, and in each case reported the formation of a dihydro-compound, although without precise statement as to quantity. The most comprehensive claim concerning the formation of dihydro-compounds is, however, that advanced by Farmer and Galley (J., 1932, 430), who, also using platinum, have described a quantitative investig-ation of the products of reduction of vinylacrylic, sorbic, α-methylsorbic, and βδ-dimethyl-sorbic acids. In each case the formation of at least two dihydro-compounds is reported, and analytical data for the proportions in which these are present in the mixtures obtained after the absorption of one molecular proportion of hydrogen are given.

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The present work was commenced with the theoretical preconception (see p. 887) that, in the catalytic reduction of conjugated unsaturated substances, the formation of considerable quantities of dihydro-products would not be the general rule. The work of Lebedev and Yakubchik being at that time the only contrary indication, we undertook a study of the compositions of partly hydrogenated butadiene derivatives by ordinary analytical methods. Platinum was employed as catalyst throughout, and ethyl muconate was selected as the initial example because its symmetry reduces the number of possible directions of reduction and thus simplifies the analytical problem. Methods for the quantitative analysis of partly hydrogenated butadiene acids had already been developed (Burton and Ingold, J., 1929, 2022) and the extension necessary to cope with the mixtures that might have arisen from ethyl muconate are described in the experimental section. The process consists in the oxidation, which can be made substantially quantitative, of the hydrogenation product by means of ozone and hydrogen peroxide, and the estimation of the various dicarboxylic acids in the mixtures thus obtained. We find that the product of reduction of ethyl muconate with one molecule of hydrogen consists essentially of equimolecular proportions of ethyl muconate and ethyl adipate. Dihydro-derivatives could not be found, although quantities in excess of 2% of the Δ^{α}-dihydro-compound (this limit corresponding to an allowance for the solubility of a degradation product) and 0·1% of the Δ^{β}-dihydro-isomeride could, if present, have been detected.

Our results on the reduction of sorbic acid were incomplete at the time of the appearance of Farmer and Galley's publication, but were continued in view of the contrast between their results and ours in the case of ethyl muconate. According to Farmer and Galley, the product formed by hydrogenating sorbic acid with one molecule of hydrogen contains 13% of a mixture of dihydro-products, in the proportion ($\alpha\beta + \alpha\delta$)-dihydro-, 40% ; $\gamma\delta$-dihydro-, 60%. As evidence for these conclusions, they report the complete removal by distillation of sorbic acid from the hydrogenation product, the oxidation by permanganate of the residual mixture of di- and tetra-hydro-compounds, and the separation from the oxidation product of acetic, propionic,* butyric, hexoic, oxalic, and succinic acids. We have carried out similar experiments, employing both our own quantitative methods and also the procedure recommended by Farmer and Galley. We cannot confirm the formation of either propionic, butyric, or succinic acid. Our mixture of monobasic oxidation acids on distillation split up completely into acetic and hexoic acids without intermediate fractions. In our treatment of the dibasic acids, 0·1% of succinic acid could, if present, have been detected. Moreover, malonic acid, which under our oxidation conditions does not undergo further degradation, could not be found, and in this case also 0·1% would have been detectable. Of the three acids which we did obtain, *viz.*, acetic, oxalic, and hexoic, the first two arose from the presence of unchanged sorbic acid, which we were unable to remove completely from the hydrogenation product by distillation ; the last is, of course, the tetrahydro-compound. Our observations, therefore, lead to the conclusion that the absorption of one equivalent of hydrogen by sorbic acid gives substantially an equimolecular mixture of this substance and its tetrahydro-derivative. Δ^{α}-Dihydrosorbic acid may possibly be formed in traces, but no considerable proportion (*e.g.*, 5—10%) of this or of total dihydro-products can be present.

The hydrogenation of β-vinylacrylic acid was next examined, since Muskat and Knapp report definite dihydrogenation and Farmer and Galley record the presence of as much as 36% of dihydro-compounds in the product of reduction by one molecule of hydrogen. The composition ascribed by the latter authors to the dihydro-mixture is $\alpha\beta$-dihydro-, 23% ; $\gamma\delta$-dihydro-, 77%. In support of these data they describe the isolation, after removal of unchanged vinylacrylic acid and oxidation of its mixed reduction products, of propionic, valeric, oxalic, and succinic acids. In our study of the reduction of vinylacrylic acid, we have used only our own methods of oxidation and analysis, and the latter is concerned with the dibasic acid oxidation products. We find, however, that succinic acid is absent, as

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* Acetic and propionic acids are described as being isolated together in approximately equal proportion, and the propionic acid is stated to have been identified qualitatively. The nature of the test applied is not specified.

also is malonic acid; 0·1% of either dibasic acid could, if present, have been detected. We confirm the formation of oxalic and valeric acids, but in our experiments the former of these arises from unchanged vinylacrylic acid, which we were unable completely to remove from the valeric acid. Actually, the formation of the Δ^{α}-dihydro-derivative in traces amounting at most to 3% is not excluded by our results, but the production of this substance in quantities comparable with the proportion claimed by Farmer and Galley (28%) is not confirmed; the other possible dihydro-compounds can definitely be stated to be absent. Thus, in this case also, we find no evidence of the formation of considerable amounts of dihydro-compounds.

Farmer and Galley have recently stated (*Nature*, 1933, **131**, 60) that the proportions in which hydrogenation products are formed from butadiene derivatives are dependent on the age of the platinum catalyst. We have studied the reduction of sorbic acid, using both fresh and aged preparations of catalyst, without alteration in the nature of the result.

It is admitted that three examples are too few to justify generalisation concerning the non-appearance of dihydro-products, and the other cases in which dihydro-compounds have been claimed by the investigators mentioned above are being re-examined. It is possible, nevertheless, to consider the mechanism underlying the type of result which so far has been our uniform experience. Two alternatives present themselves: either there is but a single reaction leading directly to the tetrahydro-derivative, or the dihydro-compound is produced as an intermediate product in two consecutive reactions, of which the second proceeds very much more rapidly than the first. As a test of the second possibility, we have measured the velocity of reduction under identical conditions of ethyl muconate and of its Δ^{α}- and Δ^{β}-dihydro-derivatives; the dihydro-compounds, far from being hydrogenated much more rapidly, were actually reduced somewhat more slowly than was ethyl muconate itself. Similarly, we have measured the rate of reduction of sorbic acid and of the mixture of dihydrosorbic acids obtained from sorbic acid by reduction with sodium amalgam in alkaline solution (Burton and Ingold, *loc. cit.*); in this case also the dihydro-compounds were hydrogenated more slowly than the butadiene acid. These results are most easily explained by the assumption that complete hydrogenation proceeds as a single reaction without the intermediate formation of free dihydro-products.

The results of this research have given us no cause to modify the theoretical views concerning catalytic reduction expressed two years ago (*Chem. and Ind.*, 1931, **50**, 1021). The electrode properties of platinum (low hydrogen over-potential) are correlated with its capacity to absorb electrons from molecular hydrogen until, in the absence of a reducible substance, the decomposition of hydrogen ceases owing to the negative charge accumulated by the metal; thus, in reduction, each platinum particle acts as a minute hydrogen electrode. The function of a simple or conjugated unsaturated substance is regarded as that of an electric lead which, by permitting the electromeric conduction of electrons from the metal, allows the decomposition of hydrogen to continue. The conduction of electrons will evidently lead to the binding of protons by the reducible substance, and in this process the unsaturated chain will lose its conductivity atom by atom, beginning preferentially at the end remote from the point of attachment to the metal. During the process of conduction, the unsaturated substance may be considered to be linked to the metal by forces analogous to those of covalency, and, external activation apart, the organic molecule will become free only when these forces vanish as the last of the conductivity of the system disappears. The applications are obvious: the formation of pinacol-like bimolecular reduction products, and of dihydro-derivatives of butadienes, would each require the liberation of the unsaturated system before its conducting power is exhausted, and these results are therefore not normal in catalytic reduction. It is proposed in a later communication to illustrate, by reference to electrolytic reduction, some of the differences between hydrogenation by dissolving metals and by hydrogen in the presence of metallic catalysts.
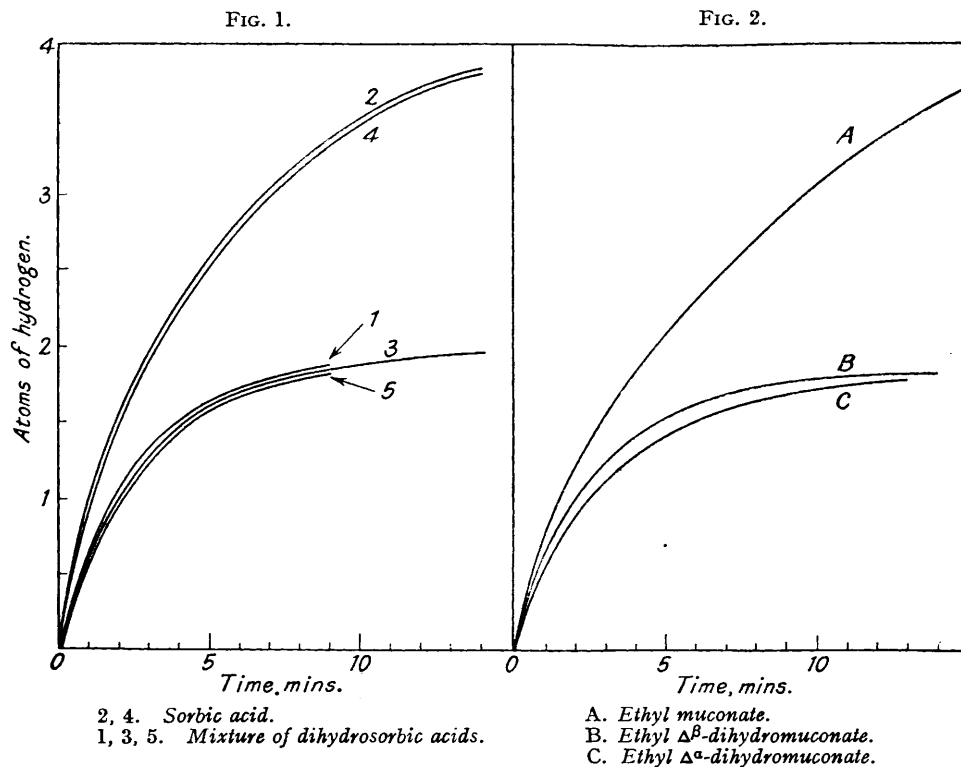
EXPERIMENTAL.

General Methods.—The method of preparing the platinum catalyst and of conducting the hydrogenations was based closely on the description given by Adams (" Organic Syntheses,"

VIII, 10, 92). Measurement of the hydrogen supply was carefully controlled, so that the apparatus could be used for estimation of unsaturation and for investigations on the rate of absorption of the gas. Oxidation of the hydrogenation products was effected by successive treatment with ozone and hydrogen peroxide (Burton and Ingold, *loc. cit.*), and in the present applications was substantially quantitative. The analytical problem resolved itself into the estimation of oxalic, malonic, and succinic acids in mixtures of all three, possibly containing adipic acid in addition. So far as concerns oxalic and succinic acids, the ground has already been covered (*idem, ibid.*). Malonic acid presented difficulty; it could not be estimated by the evolution of carbon dioxide at 160° because in the presence of oxalic acid the volume of gas liberated was much too large. Bromination and iodometric estimation of the excess of halogen, or bromination followed by removal of the free bromine by means of phenol, was precluded by the reactivity of bromomalonic acid towards reagents for halogens. Under ordinary conditions direct titration with bromine was rendered inaccurate by the volatility of the halogen and the small speed of reaction. But it was found that in the presence of hydrogen chloride bromination could be sufficiently accelerated to yield accurate results by the method of direct titration in chloroform solution. Many control experiments showed that each of these three acids could be estimated in the mixtures mentioned to within a few tenths %. In the case of succinic acid, the general method fails when the quantity present is below 2% ; but whereas in two of the three applications described below malonic and adipic acids were entirely absent, much smaller quantities could be estimated by isolation after the complete removal of oxalic acid as its calcium salt.

Ethyl Muconate.—Hydrogenation was effected in ethyl alcohol (19·8 g. in 250 c.c.) at room temperature by 1 mol. of hydrogen in the presence of platinum derived from freshly prepared hydrated oxide (0·1 g.). The product was distilled, b. p. 130—132°/14 mm., with a column, and, although it was found impossible thus to remove ethyl muconate completely without the loss of hydrogenation products, yet a considerable proportion could be eliminated by two distillations without any such loss. The distilled product was ozonised in chloroform, and the viscous ozonide decomposed with water after removal of the solvent. The product was further oxidised with hydrogen peroxide, saponified with potassium hydroxide, and the potassium salts obtained by evaporation were dissolved in water and made up to a standard volume. The appearance of any yellow colour after saponification indicated incomplete oxidation, and in the final series of experiments the solutions of potassium salts were colourless. Separate portions of this solution were taken for the estimation of oxalic, malonic, and succinic acids. Malonic acid was absent. Succinic acid was not present in excess of the amount corresponding to the correction necessary for the solubility of barium succinate; this quantity is equivalent to 2·3 mols.% as a maximum for the proportion of Δ^α-dihydromuconic ester possibly formed by hydrogenation. The amount of oxalic acid was equivalent to 10·7% of unaltered ethyl muconate in the distilled hydrogenation product, and, to within the limits of experimental error, this was the same as the quantity, 10·4%, and, in a duplicate experiment, 9·6%, retained in the distillate, when an artificial equimolecular mixture of ethyl muconate and ethyl adipate was distilled under the same conditions. The figure for the proportion of ethyl muconate in the distilled hydrogenation product was confirmed by an estimation of unsaturation, which, when calculated in terms of ethyl muconate, amounted to 11·7%, and, in a duplicate hydrogenation, 10·9%. In the latter case, a further distillation, in which the first portion of the material was collected separately, reduced the amount of ethyl muconate in this fraction only to 7·7%, and a similar further distillation of the distillate from the duplicate artificial mixture diminished the content of ethyl muconate to 7·9%. Thus it appears impossible quantitatively to separate ethyl muconate from ethyl adipate under the conditions of distillation employed, and the proportion of oxalic acid obtained in the oxidations is identical, to within the limits of reproducibility, with that which corresponds to the amount of ethyl muconate retained in the distillates.

Sorbic Acid.—Hydrogenation was carried out as in the previous example, and the distilled product, b. p. 106—108°/15 mm., was treated with ozone and hydrogen peroxide as already described, the saponification being omitted. Analysis showed that malonic acid was absent, and that succinic acid was not present in excess of the amount corresponding to the correction for solubility. It was subsequently shown by eliminating the oxalic acid as its calcium salt, isolating the remaining acids, and removing hexoic acid in a vacuum desiccator over potassium hydroxide, that succinic acid was definitely absent. The proportion of oxalic acid corresponded to the presence of 8·8% of sorbic acid in the distilled reduction product, and an estimation of unsaturation calculated in the same form gave the figure 9·7%. An artificial mixture of equimolecular proportions of sorbic and *n*-hexoic acids on distillation under similar conditions was shown by measurement of its unsaturation towards hydrogen to contain 7·8% of sorbic acid.

The above is typical of our standard procedure, but closely similar results were obtained by using in place of fresh catalyst a preparation 6 months old, which had been used before and had lost much of its original activity. We have also replaced our own method of oxidation by that used by Farmer and Galley; the hydrogenation product, distilled as before, was oxidised with permanganate in the manner recommended by these authors, and the monobasic acids were isolated and distilled. Two fractions only were obtained, *viz.*, acetic acid, b. p. below 70°/12 mm., and hexoic acid, b. p. 96—100°/12 mm. The acetic acid was not quite dry, but was shown to be free from homologues by neutralisation with silver oxide and analysis of the *whole* silver salt thus produced (Found : C, 14·6; H, 2·0; Ag, 64·6. Calc. : C, 14·4; H, 1·8; Ag, 64·7%). The *n*-hexoic acid was identified by its b. p. and by titration (Found : M, 115. Calc. : M, 116). Estimation of the dibasic acids gave results substantially identical with those already illustrated, malonic and succinic acids being absent, and the proportion of oxalic acid being identical with that retained after distillation of an equimolecular mixture of sorbic and hexoic acids to within the limits, probably about 2%, of reproducibility of the conditions of distillation.

Fig. 1.

Fig. 2.

2, 4. *Sorbic acid.*
1, 3, 5. *Mixture of dihydrosorbic acids.*

A. *Ethyl muconate.*
B. *Ethyl Δβ-dihydromuconate.*
C. *Ethyl Δα-dihydromuconate.*

β-*Vinylacrylic Acid.*—This acid was hydrogenated, the product oxidised, and the dibasic acids formed by oxidation analysed in accordance with the standard procedure already described. Malonic and succinic acids were entirely absent, but oxalic acid was found in quantity corresponding to the presence of 23% of vinylacrylic acid in the distilled hydrogenation product. The corresponding control experiment, in which an equimolecular mixture of vinylacrylic and *n*-valeric acids was distilled under identical conditions, yielded a product containing 21% of vinylacrylic acid. The results of other experiments and controls, including measurements of unsaturation, lie wholly within the range of 21—25% for the content of β-vinylacrylic acid.

Rates of Hydrogenation.—These hydrogenations were carried out, using 0·001 g.-mol. of the unsaturated substance dissolved in 100 c.c. of alcohol, at 18° and 760 mm. in a vessel shaken at a rate of 135 oscillations per minute. In the cases of sorbic acid and the mixture of dihydrosorbic acids formed from sorbic acid by reduction with sodium amalgam in alkaline solution, the platinum used was derived from 0·01 g. of freshly prepared hydrated oxide; whilst, in the examples of ethyl muconate and its Δα- and Δβ-dihydro-derivatives, the amount of platinum oxide employed was 0·05 g. The reproducibility of the observations was controlled by carrying

out experiments in which the unsaturated substances under comparison were employed alternately.   This is illustrated in relation to sorbic acid and the mixture of dihydrosorbic acids in Fig. 1, in which the numbers attached to the curves indicate the chronological order of the experiments.   Other closely consistent curves are omitted in order to avoid confusing the diagram, for which reason also the actual observations which were made at half-minute intervals throughout the range of the diagram are not shown in the usual way as circles;   the curves are, however, drawn through the observational points and are not smoothed.   Fig. 2 shows representative curves for the rate of hydrogenation of ethyl muconate and its Δ^α- and Δ^β-dihydro-derivatives;   in these cases, the observations were taken at one-minute intervals.

It can be calculated from the curves that, if the hydrogenation of either butadiene derivative were a two-stage process in which the intermediate dihydro-compound or mixture of compounds undergoes further reduction with the velocities illustrated, then, after the absorption of one mol. of hydrogen, dihydro-derivatives should be present in proportions of the order of 50%.

Ethyl Δ^α-dihydromuconate, prepared from the acid by way of its chloride, had b. p. 125—126°/14 mm. (Found : C, 59·5; H, 8·3. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%).