52. *Properties of Conjugated Compounds. Part XV. The Catalytic Hydrogenation of Butadiene-α-carboxylic Acids.*

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THE work of Lebedev and Yakubchik (J., 1928, 823, 2192) on the catalytic hydrogenation of the simple butadienoid hydrocarbons provided definite ground for believing that the butadienes can add hydrogen in all the theoretically possible ways, namely, at the $\alpha\beta$-, $\alpha\delta$-, $\gamma\delta$-, and $\alpha\beta + \gamma\delta$-positions in the molecule. The evidence was derived from the change in the rate of addition as hydrogenation proceeded, and although the shape of the absorption curves (actually absorption increment–time curves) in which the results are expressed might conceivably vary considerably with change in conditions (especially with change of temperature), there appears good ground for provisionally accepting the conclusion that the course selectively pursued during hydrogenation is traceable with fair accuracy in the form of the curves expressing absorption rates at room temperature.

In the hydrocarbon series, direct assessment of the accuracy and uniqueness with which purely constitutive characteristics are reflected in the recorded data is difficult by chemical methods—at any rate by the usual degradative methods, which at present offer the most promising alternative to Lebedev and Yakubchik's pro-

cedure. In the butadiene-α-carboxylic acid series, however, the process of degradative analysis offers less difficulty owing to the greater ease with which the oxidation fragments may be isolated : consequently the chemical method has been used to check the conclusions derived from the absorption data. The present results concern only the chemical method of analysis, but it is hoped to compare later the conclusions reached from both methods with respect to the additive capacities displayed during the first *half* of the complete hydrogenation (saturation) process.

The degradative method of analysis has been tested in the following instances : β-vinylacrylic acid, sorbic acid, α-methylsorbic acid, and βδ-dimethylsorbic acid. Each of these substances has been treated in the presence of a colloidal platinum catalyst with one molecular proportion of hydrogen at room temperature and atmospheric pressure. The proportion of the products has been determined partly by a purely separative procedure but mainly by resort to oxidation, and for the latter, experience has shown that regulated permanganate oxidation is more reliable and informative than ozonolysis in the case of unsaturated carboxylic acids. In general, each reduction product may contain four different reduced acids (geometrical isomerides being left out of consideration) and unchanged material : after separation of the latter, each of the dihydroacids in the residue will yield at least two fragments on oxidation, and these oxidation products will require separation from a quantity of fully reduced acid which is exactly equivalent to the amount of the separated unreduced acid.

The approximate proportions of the substances obtained from each of the four acids are shown in the table, the prefixes denoting the positions of the hydrogen atoms and not those of the double bond.

Composition of the Hydrogenation Products of Butadiene-α-carboxylic Acids (%).

Components of reaction product.	β-Vinylacrylic acid.†	Sorbic acid.	α-Methyl-sorbic acid.	βδ-Di-methyl-sorbic acid.
Unreduced acid	31·8	43·7	26·3	26·2
Tetrahydro-acid	31·8	43·7	26·3	26·2
αβ-Dihydro-acid	8·4* (0—18)	} 5·1* (40—55)	—	— (38)
αδ-Dihydro-acid	0 ‡ (82—100)	(45—60)	26·0*	13·6* (62)
γδ-Dihydro-acid	28·0 (0)	7·5 (0)	21·4	34·0 (0)

* These figures are obtained by difference.

† In a recent paper by Muskat and Knapp (*Ber.*, 1931, **64**, 779) this acid has been described as suffering γδ-addition during catalytic hydrogenation.

‡ It is possible that a very small amount of this acid is produced, since it cannot be asserted that no trace of acetic acid was present in the oxidation product.

In one instance, owing to the occurrence of one of the products in quantity comparable in magnitude with the experimental error, it has not been possible to give more definite information than that expressed by the total of two dihydrogenation products.

The modes of addition disclosed by these figures are radically different from those deduced from the results of reduction by metals in aqueous or alcoholic media. The figures for the latter, so far as they have been determined, are shown in parentheses (Evans and Farmer, J., 1928, 1644; Burton and Ingold, J., 1929, 2022); they are calculated on the basis of the material which actually suffers hydrogenation, and vary somewhat in accordance with the p_H value of the reducing media employed in their determination.

The type of reaction in the catalytic hydrogenation process is presumably analogous to bromine or chlorine addition (so far as the purely chemical inter-relationships of unsaturated compound and addendum are concerned)—differing from these in requiring catalytic acceleration. The carboxyl group plays no special part in the mechanism of hydrogenation, such as occurs in so-called nascent reduction, but the polar influence of this group contributes, in some measure, to the determination of additive mode, as it does during halogen addition to the butadiene acids (von Auwers and Heyna, *Annalen*, 1923, **434**, 140; Farmer and Healey, J., 1927, 1060; Muskat, Becker, and Lowenstein, *J. Amer. Chem. Soc.*, 1930, **52**, 326; Muskat and Becker, *ibid.*, p. 812). Some idea as to the extent of this influence is probably to be gathered in the instances of sorbic acid and β-vinylacrylic acid by comparing the percentages expressing the differential additive tendencies for the acids with those expressing the same tendencies for the corresponding hydrocarbons (piperylene and butadiene, respectively); the figures for the latter (50% hydrogenation) can be read off from Lebedev and Yakubchik's hydrogenation curves (*loc. cit.*, pp. 2199, 2022) and are shown in the table below.

Additive Mode (%).

Additive type.	Butadiene.	Piperylene.
No addition	33	32
$\alpha\beta\gamma\delta$-Addition	33	32
$\alpha\delta$- ,, ...	10	} 27
$\gamma\delta$- ,, ...	} 23	
$\alpha\beta$- ,, ...		9

The detailed analysis of the figures relating to the two series of conjugated compounds must await the compilation of a more complete set of data. One point in connexion with the present series of observations is, however, specially to be noted. In halogen addition it is usually possible to choose conditions under which the formation of tetrahalogenated products is suppressed until dihalogen-

ation is complete : in catalytic hydrogenation, on the other hand— whether owing to the small atomic size of hydrogen in comparison with chlorine or bromine, or for other reasons—there seems to be no doubt that the simultaneous, or rapidly consecutive, saturation of both ethylenic bonds is a characteristic and unpreventable reactivity.

EXPERIMENTAL.

The Hydrogenation Process and Methods of Estimation.—The hydrogenation vessel was a Pyrex flask shaken at the rate of 120—150 oscillations per minute. The catalyst consisted of 0·1 g. of the platinum oxide, PtO_2,H_2O (" Organic Syntheses," VIII, 10, 92); the medium was alcohol (200 c.c). The hydrogen supply was so adjusted that the rate of absorption of the well-washed gas could be accurately followed from minute to minute. All hydrogenations were conducted at atmospheric pressure.

When reduction was complete the catalyst was coagulated and filtered off, and the alcohol removed under reduced pressure. The reaction product was distilled carefully from a bath maintained at a temperature a little lower than the boiling point of the conjugated acid in use : in this way practically all of the unchanged acid remained in the distilling flask. A second distillation was usually carried out, and the small residue of conjugated acid (if any) added to the first; the weight of this second residue, when deducted from the weight of the original distillate, gave the yield of reduction product.

The liquid distillate was oxidised with 3% permanganate solution under suitable conditions relating to dilution, efficient stirring, and slow addition of permanganate. From the amount of permanganate decolorised at 0° a close estimate of the amount of saturated and ethylenic matter present could usually be made. The oxidation products were recovered as completely as possible and very carefully fractionated. In all cases they were quite saturated towards the permanganate and for the greater part consisted of simple fatty acids. Samples from the various fractions of the distilled addition products were usually titrated with $N/20$-baryta in order to obtain the average molecular weight of the components of each sample.

The estimation of the amount of oxalic acid produced during the oxidation of the hydrogenation product would seem to afford a direct method of determining the amount of conjugated acid which survives oxidation; ordinarily the conjugated acid (except in the case of $\alpha\beta$-, $\alpha\gamma$-, or $\alpha\beta\gamma$-polyalkyl-acids) should give rise to one or two molecules of oxalic acid provided that oxidation at the ethylenic linkages is complete and proceeds to the customary stage for each fragment. Usually, however, the conjugated acid, in spite of the

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fact that it decolorises the anticipated quantity of permanganate at 0° (*e.g.*, the equivalent of 8 atoms of oxygen in the case of sorbic acid), fails to yield the full quantity of oxalic acid.* When Δ^α-acids are produced by reduction, they, on the other hand, give nearly quantitative yields of oxalic acid, and the figures so obtained may be utilised in the estimation of the Δ^α-acids, provided that all the initial conjugated acid has been removed from the hydrogenation mixture.

Pyruvic acid, obtainable from α-methylsorbic acid and its $\gamma\delta$-addition product, was estimated by the method of Maclean (*Biochem. J.*, 1913, **7**, 611). Being easily decomposed, it was necessary to estimate it in the aqueous solution immediately after the oxidation : indeed, its presence in the finally fractionated oxidation product could not be detected by either phenylhydrazine or *p*-nitrophenylhydrazine.

Since in all cases exactly one molecular proportion of hydrogen per molecule of conjugated compound was employed, the quantity of unchanged acid in the reduction product should exactly equal the amount of acid that suffered complete saturation. Generally the amount of saturated material could be fairly closely calculated from the quantity of permanganate solution decolorised at 0° by the ethylenic constituents of the hydrogenation product, but in the case of $\beta\delta$-dimethylsorbic acid the oxidation products comprised *inter alia* acetoacetic acid (from the Δ^β-dihydro-acid), which readily suffered further oxidation, thus increasing the amount of permanganate decolorised : in this case the amount of saturated acid actually isolated was of course in excess of that deduced from the quantity of permanganate taken up. Where the figures for the proportion of saturated acid (as obtained respectively by direct weighing and by calculation from the amount of permanganate decolorised) differ somewhat, the higher value is recorded in the table of percentages.

Hydrogenation of Sorbic Acid.—Expt. 1. From 5·6 g. of sorbic acid, 2·2 g. (39·3%) of unchanged acid were recovered. The distillate (see above) was oxidised and the following acids were identified qualitatively : acetic, propionic, butyric, hexoic, and oxalic. This indicated that the following types of addition had occurred : $\alpha\beta$, $\alpha\delta$, $\gamma\delta$, and $\alpha\beta\gamma\delta$. A small amount of succinic acid was isolated in a subsequent experiment, so completing the number of degradation products which could normally arise.†

* The nature of the products actually obtained has not been discovered, but the whole question of the hydroxylation of conjugated compounds by permanganate and similar reagents is at present under investigation.

† Acetic acid could be formed from $\Delta\gamma$-dihydrosorbic acid ($\alpha\beta$-addition) and also from the malonic acid to be expected from $\Delta\beta$-dihydrosorbic acid ($\alpha\delta$-addition). Succinic acid could arise only from the product of $\alpha\beta$-addition, *i.e.*, from the $\Delta\gamma$-dihydro-acid.

Expt. 2. From 11·2 g. of sorbic acid employed, the unchanged acid amounted to 4·8 g. (41·7%) and a sample (3·4 g.) of the distillate took up an amount of permanganate corresponding to the presence of 0·7 g. of hexenoic acid; from these figures the amount of sorbic acid converted into hexoic acid was 4·9 g. (43·7%). Fractionation of the oxidation products yielded the portions (i) 0·1 g. of acid, b. p. below 75°/12—14 mm., (ii) 0·3 g., b. p. 75—82°/12—14 mm., and (iii) 1·0 g., b. p. 88—103°/12—14 mm. Distillation of the remaining material was discontinued because oxalic acid began to separate in the distilling flask. The average molecular weights of the portions (i), (ii), and (iii) were determined by titration : for (i) the value M, 69 was found, indicating that approximately 50% of acetic acid and 50% of propionic acid were present; (ii) consisted of butyric acid (Found : M, 87. Calc. : M, 88); (iii) consisted of slightly impure hexoic acid (Found : M, 110. Calc. : M, 116). The undistilled residue was washed into a dish and kept in a vacuum desiccator for several days. The solid which separated was pure oxalic acid, which was estimated in the usual way by titration of a hot acidified solution of the residue with $N/10$-permanganate. The cooled oxidation liquor was thoroughly extracted with ether and from the extract a minute quantity of slightly impure succinic acid (identity confirmed by comparison with an authentic specimen) was isolated. The oxalic acid content of the oxidation product was 0·36 g., corresponding to 7·5% of the $\gamma\delta$-addition product; the amount of succinic acid was too small and its method of isolation too imperfect to warrant the quoting of a definite percentage yield.

Expt. 3. From 5·6 g. of sorbic acid submitted to hydrogenation, the recovered acid amounted to 2·3 g. (41·1%).

Expt. 4. In this experiment, in which 5·6 g. of sorbic acid were initially employed, the oxalic acid produced by oxidation was precipitated as the barium salt. Owing to the incompleteness of formation of oxalic acid, however, the yield of the salt gave no true indication of the percentage of conjugated acid. The portion of the oxidation product consisting of fatty acids was obtained in good yield and was divided into the fractions : (i) 0·2 g., b. p. below 75°/13 mm., (ii) 0·3 g., b. p. 75—82°/13 mm. (M, 89); (iii) 1·9 g., b. p. 88—104°/13 mm. (M, 112·5). There was a very small gummy residue. The values of M obtained for (ii) and (iii) corresponded so closely to the molecular weights of butyric and hexoic acids that a fairly complete separation seemed to have been obtained.

The figures obtained in Expts. 1—4 form the basis of the table of percentage composition given on p. 431.

Hydrogenation of α-Methylsorbic Acid.—*Expt.* 1. 12·6 G. of the acid gave, after hydrogenation, 3·0 g. of unchanged acid and a

liquid acid mixture. A known weight of the latter was carefully oxidised with permanganate at 0° in order to estimate the percentage of methylhexenoic acids present and thence to calculate the amount of methylhexoic acid present. It was estimated in this way that the hydrogenation product contained 3·3 g. (26·4%) of saturated acid. The residual acid mixture was distilled and three fractions were collected : (i) 1 g. of acid, b. p. below 75°/12—14 mm. (Found : M, 80·1), which undoubtedly consisted of propionic and butyric acids with possibly some acetic acid, (ii) 1·1 g., b. p. 75—82°/12—14 mm. (Found : M, 89·7), which was almost pure butyric acid, and (iii) 1·1 g., b. p. 80—108°/12—14 mm. (Found : M, 110), which consisted largely of α-methylhexoic acid but contained some butyric acid. There was a small gummy residue after distillation. The pyruvic acid formed had decomposed and was not identified in this experiment.

Expt. 2. 6·3 G. of acid yielded after hydrogenation 1·55 g. (24·2%) of unchanged acid and a product which was estimated (by permanganate oxidation) to contain 1·7 g. (26·1%) of fully reduced acid. Pyruvic acid was not identified.

Expt. 3. 6·3 G. of the acid, after hydrogenation, were oxidised with permanganate without previous distillation. The filtered reaction mixture readily yielded the phenylhydrazone of pyruvic acid (m. p. 178°; mixed m. p. 177—179°) on treatment with phenyl-hydrazine acetate. The amount of pyruvic acid present in an aliquot part of the mixture was estimated by the method of Maclean (*loc. cit.*), and the oxalic acid contained in the remainder was pre-cipitated as its barium salt. The pyruvic acid content of the oxidised hydrogenation product as thus estimated was 2·1 g., corresponding to a total proportion of unchanged acid and γδ-di-hydrogenated acid (both substances being potential sources of pyruvic acid) of 47·7%. By difference between this figure and the percentage of fully saturated acid present, the proportion of γδ-di-hydro-acid formed during hydrogenation was found to be 21·4%. This figure expresses, of course, only a lower limit, but there is no reason to suppose that it is seriously in deficit of the true figure.

The mother-liquor from which the barium oxalate had been precipitated yielded a mixture of liquid acids which gave the fractions : (i) 1·3 g., b. p. below 75°/12—14 mm., which consisted of a mixture of propionic acid and acetic acid (Found : M, 70·8) apparently in the proportion of 77% of the former and 23% of the latter, (ii) 0·8 g., b. p. 75—83°/12—14 mm., consisting of almost pure butyric acid (Found : M, 89·7. Calc. : M, 88), and (iii) 1·0 g., b. p. 90—108°/12—14 mm. (Found : M, 130·1. Calc. : M, 132), consisting of almost pure α-methylhexoic acid. No methylsuccinic acid could be isolated by the method used previously for succinic acid

and therefore no, or only an insignificant amount of, αβ-hydrogenated product had been formed. The approximate composition of the hydrogenation mixture deduced from these figures is shown on p. 431. It should be noted that the proportion of propionic acid (77%) in the propionic acid–acetic acid mixture (as estimated from the basicity) would correspond to the occurrence of αδ-dihydrogenation of the original acid to the extent of 20%, provided the whole of the methylmalonic acid which would be expected as the complementary oxidation product of propionic acid suffered conversion into propionic acid.

Hydrogenation of βδ-*Dimethylsorbic Acid.*—*Expt.* 1. 7·0 G. of the acid gave, after hydrogenation, 1·86 g. (26·2%) of unchanged acid. From the amount of permanganate required to oxidise the hexenoic acids produced, it was estimated that 1·6 g. (22·6%) of the original acid had been reduced to βδ-dimethylhexoic acid. The permanganate oxidation resulted in the formation of a strongly-smelling ketone and (presumably) acetoacetic acid. The latter, however, did not withstand further oxidation to acetic and oxalic acids : consequently the quantity of permanganate decolorised afforded no reliable guide to the proportion of hexenoic acids, and therefore hexoic acid, originally present. The ketone was removed by steam distillation and shown to be methyl *sec.*-butyl ketone ; it was free from acetone, and its semicarbazone melted at 134° (mixed m. p. with a specimen derived by the reduction of mesityl oxide, 133—134°).

The remaining portion of the oxidation product was worked up in the usual way and distilled. Three fractions were collected : (i) 0·2 g. of an acid, b. p. below 75°/12—14 mm., (ii) 0·35 g., b. p. 78—86°/12—14 mm., which was somewhat impure *iso*butyric acid, and (iii) 0·6 g., b. p. 88—110°/12—14 mm., which was almost pure βδ-dimethylhexoic acid (Found : M, 140. Calc. : M, 144). Of other theoretically possible products, a little acetic acid was present but neither acetone nor methylsuccinic acid could be detected in even small proportion.

Expt. 2. The hydrogenation product from 0·7 g. of the acid was oxidised without previous distillation, and the oxalic acid precipitated as the barium salt, after removal of the methyl *sec.*-butyl ketone which had been formed, by steam distillation. The amount of ketone obtained was 1·7 g., representing a 34% yield of the γδ-dihydro-acid. The estimation of the oxalic acid formed by the oxidation of the unsaturated acids proved again to be unreliable as a guide to the combined amounts of unchanged acid and γδ-dihydro-acid present. The product was fractionated as before, giving (i) 0·2 g., b. p. below 75°/12—14 mm., which consisted of acetic acid and some *iso*butyric acid (Found : M, 66), (ii) 0·4 g. of *iso*butyric

acid, b. p. 75—85°/12—14 mm. (Found : M, 86. Calc. : M, 88), and (iii) 0·9 g., b. p. 88—110°/12—14 mm., consisting of βδ-dimethyl-hexoic acid (Found : M, 140. Calc. : M, 144).· The deduced percentage composition of the hydrogenation mixture is shown on p. 431.

Hydrogenation of β-*Vinylacrylic Acid.*—*Expt.* 1. 4·9 G. of the acid, dissolved in 150 c.c. of alcohol, were submitted to reduction. The unchanged acid was separated from the more volatile products by slow distillation as before, but in this case it invariably polymerised during the distillation ; the polymerised acid, which retained a little of the reduced material, amounted to 1·9 g. A portion (2·75 g.) of the distillate was oxidised with permanganate and the following acids were isolated : propionic, oxalic, valeric, and succinic. From the quantity of permanganate decolorised at 0°, it was estimated that the amount of saturated material (valeric acid) formed during the hydrogenation was 1·6 g., accounting for 32·5% of the conjugated acid initially employed. The percentage of unchanged vinylacrylic acid would then be 32·5%. Titration of an aliquot part of the acidified permanganate oxidation product with N/10-permanganate at 60° indicated an oxalic acid content of 1·2 g. for the *whole* of the oxidation product; this corresponds to a content of 1·3 g. of $Δ^α$-pentenoic acid in the hydrogenation product and shows that 27·5% of the conjugated acid suffered γδ-addition of hydrogen.

The oxidation product on distillation gave the fractions : (i) 0·4 g. of impure propionic acid, b. p. 65—75°/13—15 mm. (Found : M, 80. Calc. : M, 74), and (ii) 1·1 g. of valeric acid, b. p. 86—88°/13—15 mm. (Found : M, 102. Calc. : M, 102). A small gummy residue remained from which crystals of oxalic acid separated. This was dissolved in water, filtered, and freed from oxalic acid by oxidising the latter at 60° with permanganate. From the oxidation liquor, a small quantity of succinic acid (identity confirmed by comparison with an authentic specimen) was isolated.

The presence of acetic acid amongst the oxidation products could not be recognised in any experiment. The identification, however, of a small amount of this acid when contained in a comparatively large amount of propionic acid would of course be difficult and consequently it is quite possible that the hydrogenation product contained a small proportion of αδ-dihydrogenated material.

Expt. 2. 4·9 G. of the acid yielded, after hydrogenation and distillation, 1·8 g. of polymerised vinylacrylic acid. By oxidising 1·88 g. of the distillate with permanganate at 0°, the total amount of saturated material was calculated to be 1·5 g., corresponding to 31% of the original acid. The proportion of conjugated acid which escaped hydrogenation would then also be 31%. Titration of an

aliquot part of the acidified permanganate oxidation liquor at 60° with $N/10$-permanganate showed that the whole oxidation product contained 0·7 g. of oxalic acid, which corresponds to the formation of Δ^{α}-pentenoic acid ($\gamma\delta$-hydrogenation product) from the conjugated acid to the extent of 28·5%.

Fractionation of the oxidation product gave the fractions (i) 0·3 g. of crude propionic acid, b. p. 60—75°/12—14 mm. (Found : M, 82. Calc. : M, 74), and (ii) 0·7 g. of valeric acid, b. p. 86—90°/12—14 mm. (Found : M, 106. Calc. : M, 102).