

423. *Catalytic Hydrogenation of Unsaturated Compounds. Part III.
Selectivity of Attack in Relation to the Nature of the Catalyst.*

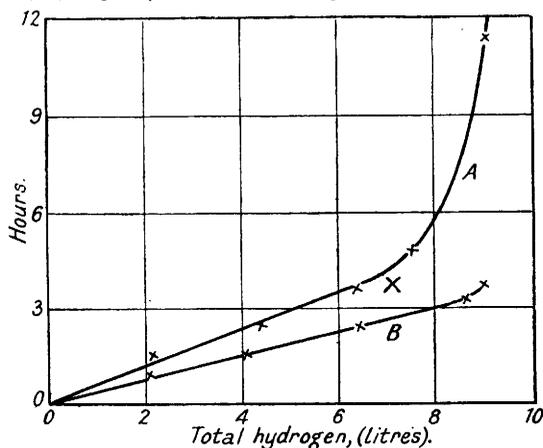
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IN a previous paper (Farmer and Galley, J., 1932, 430) it was reported that the course of hydrogenation in conjugated compounds of the sorbic acid series was materially affected by the position and number of the alkyl groups substituting the carbon chain. Subsequent examination of the influence of constitution on the additive mode showed that change in the condition or state of reactivity of the platinum catalyst employed in the earlier experiments was in itself capable of influencing the course of reaction (Farmer and Galley, J.,

1933, 687; this vol., p. 304), and the possibility presented itself that still other (possibly minor) features of the experimental method of effecting hydrogenation might affect the result and might indeed be sufficiently important to render nugatory any comparisons of the influence of constitution on the additive mode save such as were conducted under the most rigorously defined conditions of operation. These features include of course the temperature and pressure conditions employed, and in addition (a) the character of the solvent or medium, (b) the chemical nature of the catalyst, and (c) the form, condition, and concentration in which the catalyst is applied. The present work takes into consideration those influences on the course of hydrogenation specifically connected with the catalyst and the solvent, and leaves for future study the influence of the temperature and of the pressure; consequently all the results here described refer to the same temperature and pressure conditions as those employed in the earlier experiments, *viz.*, room temperature and atmospheric pressure.

Influence of Solvent.—In many types of additive reaction the solvent, for one reason or another, exerts a specific influence not merely on the speed but on the course of reaction, and indeed such an influence has already been observed definitely to affect the course of

Rate of absorption of hydrogen by sorbic acid during the first half of the saturation process.



Curve A represents the rate when 0.1 g. of platinum per 44.8 g. of acid was employed, and curve B when double this concentration was used.

hydrogenation of a polyolefinic ketone (Adkins, Diwoy, and Broderick, *J. Amer. Chem. Soc.*, 1929, **51**, 3418). To test the importance of solvent influence in determining the course of hydrogenation of simple butadienoid acids, the authors have submitted sorbic acid to 50% hydrogenation with a platinum catalyst in dry toluene, in ethyl acetate, and in water, and have compared the results with those obtained in alcohol, the medium previously employed by them. The figures expressing the course of reaction are given on p. 1935. Now, although the speed of reaction varies considerably in the different solvents, the results do not reveal any material difference in the additive mode which can be attributed to the specific character of the solvent employed; furthermore, although the speed of reaction varies, as is well known, with the proportion of solvent taken, yet neither in the present nor in any previous experiments has the proportion of solvent taken recognisably affected the additive mode.

Concentration of Catalyst.—Change in the concentration of the catalyst with respect to the conjugated compound appears quite definitely to affect the additive mode, as is shown by the figures expressing the composition of the 50% hydrogenation product of sorbic acid given on p. 1935. But the phenomenon here observed is doubtless only indirectly dependent on concentration as such, for in those cases in which a small concentration of catalyst gives a somewhat different result from that given by a larger proportion (the difference being outside the range of experimental error), the effect appears to be related to the time during

which the catalyst has been in use, rather than to its initial concentration; accordingly, small variations in concentration which do not greatly lengthen the time of reduction have not in general any recognisable effect on the additive mode. This is probably to be understood by reference to the form of the absorption curves in typical operations carried out with considerably different concentrations of the same (uniform) catalyst. The curves A and B in the figure refer to reductions in which the platinum catalyst in one case suffers serious diminution of activity after the lapse of 1—2 hours and in the other retains its activity until the end of the operation. Present indications are that change in the additive mode in such cases only begins when deterioration in the activity (*i.e.*, "ageing") of the catalyst becomes marked, as occurs at point X in curve A.

Included amongst the results on p. 1935 are figures relating to several experiments in which small amounts of carbon disulphide were added to the reaction mixture prior to reduction. Although the catalyst became progressively poisoned, no specific effect on the course of hydrogenation is apparent, save such as might have been occasioned during the later stages of poisoning by diminution in the activity of the yet unpoisoned centres of the catalyst with long-continued use, *i.e.*, with "ageing."

Nickel as Catalyst.—Experiment shows that the change from platinum to nickel as catalyst can affect the course of reaction more profoundly than can such important substitutional changes in the conjugated compound as alkylation. For the purpose of comparing the additive mode promoted by nickel with that already observed for platinum, it was necessary, in order to retain equality of working conditions, to avoid the elevated temperatures or pressures (or both) which the commonly-used preparations of nickel require. An activated form of nickel (Raney's catalyst) was found to be admirably suited to the purpose, since it proved capable of promoting the reduction of acids of the mono-, di-, and poly-olefinic series with reasonable celerity, although on the whole more slowly than does platinum derived from platinum oxide.

The following table compares the effect of employing activated nickel in the 50% hydrogenation of (*a*) sorbic acid and (*b*) sodium muconate * with that of employing platinum. The figures for platinum are quoted from the previous paper of the series (this vol., p. 307), and the figures as a whole show the extents to which the two conjugated compounds undergo conversion into their various hydrogenation products or remain unchanged. Complete (100%) resolution of the various mixtures into their component substances has not been possible on the experimental scale adopted, and for this reason and because the very different methods of determination employed necessarily vary in accuracy, the figures are to be regarded as only approximate. It is especially to be noted that no definite figure is here given for the extent of formation of $\Delta\beta$ -dihydrosorbic acid: no satisfactory method for the direct determination of this substance by separative or degradative means is available, since the acid very closely resembles its $\Delta\gamma$ -isomeride, yields no very distinctive derivatives, and on degradation with permanganate yields neither malonic acid (to be expected together with propionic acid) nor oxalic acid; accordingly, although the $\Delta\beta$ -acid appears to be an invariable and quite significant component of the hydrogenation product, for which a difference figure has been quoted in previous larger scale experiments, no direct estimate of its proportion is possible. The results obtained, however, show that, whereas the reduction of sorbic acid to the dihydro-stage approaches within measurable distance of completeness in the presence of nickel, that of sodium muconate does not; moreover, of the different dihydrosorbic acids which are produced by nickel, the $\Delta\alpha$ -form occurs by far the most extensively, and since this form crystallises well in spite of its low melting point,

* Sodium muconate is used in place of muconic acid owing to the insolubility of the latter in all ordinary media, and in preference to methyl or ethyl muconate for convenience in analysing the partial hydrogenation products. It is not impossible that the additive mode of ionised sodium muconate is somewhat different from that of muconic acid, or those of the muconic esters, especially in view of a statement by Armstrong and Hilditch (*Proc. Roy. Soc.*, 1925, **108**, 123) to the effect that the selectivity of the hydrogenation process observed by Moore, Richter, and van Arsdell (*J. Ind. Eng. Chem.*, 1917, **9**, 451) in respect of cotton-seed oil and by themselves in respect of soya bean, linseed, maize, and cotton-seed oils or their derivatives is more or less suppressed when the free acids are taken in place of the neutral esters.

the reduction of sorbic acid to the 50% stage in presence of nickel constitutes a convenient method for its preparation. Thus now for the first time a conjugated butadienoid compound has been shown to be susceptible under the influence of a suitable catalyst of a very high degree of step-wise reduction : but even with a catalyst of proved efficiency in the promotion of step-wise reduction, the high degree of selective action promoted in one example is not, generally speaking, exercised independently of the conjugated constitution, as is clear from the example of sodium muconate in which a catalyst known to be highly selective with sorbic acid promotes to an important extent non-selective reduction.

50% Hydrogenation of Sorbic and Muconic Acids (Nickel and Platinum).

Conjugated acid.		Components of reduction mixture (%).		
		Ni catalyst.		Pt catalyst.
Sorbic	Sorbic acid (unchanged)	4.0	44	
	Δ^{α} -Dihydrosorbic acid	8.30	7	
	Δ^{β} - " "	(?)	} 5	
	Δ^{γ} - " "	0.4		
	Hexoic acid	3.0	44	
	Unseparated residue (including Δ^{β} -dihydrosorbic acid) and loss	9.6	—	
Muconic (sodium salt)	Muconic acid (unchanged)	26.9	40.3	
	Δ^{α} -Dihydromuconic acid	31.6	11.3	
	Δ^{β} - " "	15.0	7.5	
	Adipic acid *	26.9	40.3	

* The figure for adipic acid is necessarily equal to that for unchanged muconic acid and is so shown in the table (also in the table on p. 1933). In practice the proportion of unchanged muconic acid could be determined directly with a considerable degree of accuracy, whereas the experimental figure for adipic acid was almost invariably low owing to the losses incurred in the rather complicated series of separative operations being almost entirely losses of adipic acid or of its ester.

In view of the fact that selective attack in sorbic acid, so far as it occurs, is mainly directed towards the reduction of the $\gamma\delta$ - rather than of the $\alpha\beta$ -double bond (and this applies whether the catalyst is nickel, platinum or, as is shown below, palladium) it might be deduced that the main cause of the difference in additive mode between sorbic acid and muconic acid is that the former contains only one $\alpha\beta$ -double bond and the latter two—in other words, that the difference is due to the unequal facility of reduction of $\alpha\beta$ -bonds on the one hand and $\gamma\delta$ -, $\epsilon\zeta$ -, etc., bonds on the other. Although a considerable difference in reducibility between double bonds adjacent to the carboxyl group and those more remote doubtless exists, yet recent experiments by one of the authors with Dr. S. R. Martin reveal that the courses of reduction pursued by certain conjugated triene and tetraene acids are not readily to be correlated with one another merely on the basis of the tendencies towards $\alpha\beta$ -reduction on the one hand and towards $\gamma\delta$ -, $\epsilon\zeta$ -, etc., reduction on the other; moreover, any explanation on these lines is complicated by the occurrence of terminal ($\alpha\delta$ -, $\alpha\zeta$ -, etc.) hydrogenation, a mode of addition which becomes important with sodium muconate.

Since the partial hydrogenation of ordinary or *trans-trans*-muconic acid (in the form of its sodium salt) yields, *inter alia*, *trans*- Δ^{α} -dihydromuconic acid, that of *cis-cis*-muconic acid should yield *cis*- Δ^{α} -dihydromuconic acid. The methyl *cis-cis*-muconate, m. p. 75°, originally described by one of the authors (Farmer, J., 1923, **123**, 2547), was accordingly submitted to 50% hydrogenation in presence of nickel, and there was obtained, together with some unchanged methyl *cis-cis*-muconate, a mixture of esters which yielded adipic acid, Δ^{β} -dihydromuconic acid, and a new unsaturated acid on hydrolysis. The last acid, m. p. 80—81°, was readily separable in a state of purity from the accompanying acids, and represented the *cis*-isomeride of the Δ^{α} -dihydromuconic acid. The experimental details of the production of this acid and the evidence for its constitution are relegated for convenience to the succeeding paper (p. 1940).

Palladium as Catalyst.—The extent of dihydrogenation which was effected during the 50% hydrogenation of sorbic acid was even greater with palladium than with nickel. Nearly complete dihydrogenation occurred with palladium employed in the following forms : (a) finely divided palladium obtained by shaking powdered palladium oxide with

hydrogen, (b) palladium supported on barium sulphate, (c) palladium supported on calcium carbonate, and (d) a platinum-carbon catalyst further activated by deposition of palladium. Three of these catalysts are well known for their efficacy in promoting specific (but different) types of reductive action, yet all agree in showing strong selective action in the reduction of sorbic acid, and two at least (the only ones tested) in the reduction of sodium muconate. The approximate extent of conversion of sorbic acid and sodium muconate into their respective hydrogenation products is shown in the table below. With palladium, as with nickel, the formation of dihydro-products from sodium muconate at the stage of 50% hydrogenation is less complete than it is with sorbic acid, and, secondly, terminal reduction of the butadiene chain of sodium muconate can reach the important figure of about 15%. Small proportions of unchanged sorbic acid and of hexoic acid have been recognised in several of the reduction mixtures.

50% Hydrogenation of Sorbic Acid and of Sodium Muconate (Palladium Catalysts).

		Product.	Pd (PdO), Pd-BaSO ₄ , Pd-CaCO ₃ , Pd-C-Pt,			
			%.	%.	%.	%.
Sorbic acid	{	Δ ^α -Hexenoic acid	86.5	89.6	75.0	77.4
		Δ ^γ - " "	2.3	1.8	8.5	5.8
		Unseparated residue (including Δ ^β -dihydrosorbic acid) and loss	11.2	8.6	9.3	16.8
Muconic acid (sodium salt)	{	Muconic acid	10.8	—	22.3	—
		Δ ^α -Dihydromuconic acid	56.3	—	40.3	—
		Δ ^β - " "	14.8	—	12.7	—
		Adipic acid	10.8	—	22.3	—
		Loss	7.3	—	2.4	—

Conclusions.—(1) Platinum, nickel, and palladium all show definite, but very different, tendencies towards the promotion of the step-wise reduction of conjugated compounds at the ordinary temperature and pressure,* and in the case of palladium step-wise reduction may attain or approach closely towards completeness.

(2) The selectivity of the catalyst does not vary greatly with the form or method of application of the particular metal employed,† but the most striking differences in promoting action appear between different metals. There is nothing in the present results, however, to preclude the possibility that a metal may be preparable in distinctive forms (*e.g.*, different crystalline forms) capable of promoting quite dissimilar modes of hydrogenation.

(3) The change from one metal, as catalyst, to another may have at least as profound an influence on the additive mode of a conjugated compound as have important structural (substitutional) modifications of the conjugated chain.

(4) Toluene, ethyl acetate, water, and alcohol, when employed as solvents in the reduction of sorbic acid with platinum, appear to have no marked specific influence on the course of hydrogenation. The concentration of the catalyst also appears to have no *direct* influence on the additive mode in the case of platinum, but "ageing" of the catalyst, with accompanying change in additive mode, is more likely to occur with low than with high concentrations.

Identification of Hydrogenation Products.—The most notable feature of the partial hydrogenation experiments was the high degree of production (contrary to previously held

* The work of Waterman and his collaborators (*Rec. trav. chim.*, 1932, **51**, 401, 653) supplies evidence of a difference in catalytic action between (a) nickel at low pressures and high temperatures on the one hand and at high pressures and the ordinary temperature on the other, and (b) platinum at the ordinary temperature and atmospheric pressure on the one hand and nickel at about 180° and atmospheric pressure on the other, in the hardening of oils containing polyolefinic glycerides. The observations of Bourguel and his collaborators on the catalytic reduction of acetylenic compounds (*Compt. rend.*, 1925, **180**, 1753; *Bull. Soc. chim.*, 1927, **41**, 1443; 1929, **45**, 1975) afford evidence of perfect selectivity on the part of palladium, although only when this is in colloidal form.

† Test experiments carried out with supported platinum catalysts indicate that with these, as with the unsupported platinum catalyst of Adams, the degree of formation of dihydro-products from sorbic acid is of a comparatively low order.

views) of dihydro-derivatives of the conjugated acids employed. Most of these dihydro-compounds can readily be obtained in pure form in considerable amounts, and all with the exception of Δ^β - and Δ^γ -dihydrosorbic acids are beautifully crystalline at room temperature and yield characteristic derivatives.

The general procedure for the separation of the hydrogenation products was that already reported in the earlier papers of this series; the forms in which the various products were weighed in determining the approximate composition of the partial reduction products are those reported below. The individual compounds were identified in the following ways:—

Unchanged sorbic acid, by isolation of the crystalline acid, m. p. 134° , mixed m. p. 134° , very sparingly soluble in boiling light petroleum.

Δ^α -*Hexenoic acid*, by isolation of the crystalline acid, m. p. 33° , mixed m. p. 33° , readily soluble in boiling light petroleum (b. p. 40 — 60°), from which it separated on cooling to 0° in large prisms; the anilide formed colourless needles, m. p. 110° , mixed m. p. 110° .

Δ^β -*Dihydromuconic acid*, by isolation of the crystalline acid, m. p. 197° , mixed m. p. 197° ; in practice the crude acid was converted by esterification with methyl-alcoholic hydrogen chloride into its methyl ester, which with bromine yielded methyl $\beta\beta'$ -dibromoadipate (colourless needles or prisms from petroleum or methyl alcohol, m. p. 93° , mixed m. p. 93°), from which methyl Δ^β -dihydromuconate, m. p. 16° , was quantitatively recoverable by treatment with zinc and methyl alcohol, and convertible by hydrolysis with dilute sulphuric acid or sodium carbonate into the corresponding Δ^β -acid, m. p. 197° (a small proportion of the low-melting form of methyl $\beta\beta'$ -dibromoadipate always accompanied the form of m. p. 93°).

trans- Δ^α -Dihydromuconic acid, by isolation of the crystalline acid, m. p. 191° , mixed m. p. 191° ; in practice the crude acid was converted by the action of methyl-alcoholic hydrogen chloride into its methyl hydrogen ester, m. p. 60° , and regenerated therefrom by hydrolysis with sodium carbonate; on oxidation with permanganate the acid yielded succinic acid and oxalic acid almost quantitatively (see succeeding paper).

cis- Δ^α -Dihydromuconic acid, obtained for the first time in the present investigation, was isolated in crystalline form, m. p. 81° , and identified by analysis and by its almost quantitative conversion into succinic acid and oxalic acid on oxidation with permanganate (see succeeding paper).

Δ^β - and Δ^γ -*Dihydrosorbic acids*, not absolutely identified as such; the presence of the latter acid in the residual portions of the partial reduction products from sorbic acid, after separation of unchanged sorbic and Δ^α -dihydrosorbic acids, was deduced from the formation of succinic acid on oxidation of the residue with permanganate; the evidence of the formation of the Δ^β -acid is discussed on pp. 1931, 1937.

Hexoic acid: the presence of this acid in small quantities in certain of the reduction products from sorbic acid was deduced from the isolation of a saturated oily acid, b. p. 200 — 206° , solidifiable on cooling to -25° , convertible on esterification with alcoholic hydrogen chloride into a saturated ester having the characteristic odour of ethyl hexoate.

Adipic acid, by isolation of the crystalline acid, m. p. 148° , mixed m. p. 148° .

EXPERIMENTAL.

A. Hydrogenation with a Platinum Catalyst.

Partial Hydrogenation of Sorbic Acid in Various Solvents.—The series of partial reductions (50%) tabulated below was carried out with the object of testing (a) the specific influence of the solvent and (b) the influence of a catalyst poison (carbon disulphide) on the course of hydrogenation at room temperature and atmospheric pressure. The platinum catalyst employed was derived as in former experiments from hydrated platinum oxide. The method of working up the product was that described previously (this vol., p. 306). Only the percentage figure for the unchanged sorbic acid contained in the reduction product is given, the total extent of conversion into dihydro-acids being theoretically equal to the difference between twice this figure and 100. The time required for 50% hydrogenation to occur is also given except in two cases in which it was not observed. The experimental error of observation arising by incomplete isolation of sorbic acid is considered to be not greater than 1%.

Expt.	Acid, g.	Catalyst, g.	Solvent.	Time, hrs.	Unchanged acid, %.	Added CS ₂ , g.
1	5.6	0.1	Alcohol (75 c.c.)	0.75	43	—
2	11.2	"	"	(?)	42	—
3	44.8	0.2	" (250 c.c.)	3.5	39	—
4	"	0.1	"	11.5	34	—
5	5.6	"	Toluene (75 c.c.)	(?)	43	—
6	"	"	Ethyl acetate (75 c.c.)	0.75	43	—
7*	"	"	Water (75 c.c.)	3.25	39	—
8	"	"	Alcohol (75 c.c.)	1.75	43	0.0010
9	"	"	"	3	43	0.00175
10	"	"	"	6	39	0.00225
11	"	"	"	> 8 †	‡	0.0025

* Sodium sorbate was employed in this experiment.

† Reaction ceased after 8 hours, and only 0.2 mol. of hydrogen had then been absorbed.

‡ Major proportion unchanged.

B. Hydrogenation with a Nickel Catalyst.

Partial Hydrogenation of Sorbic Acid in Alcohol.—The active form of nickel known as Raney's catalyst (prepared by dissolving the aluminium from a nickel-aluminium alloy containing 50% of each component) was suitable for the promotion of the hydrogenation at room temperature and atmospheric pressure of a variety of conjugated (tetraene, triene, and diene) and ethylenic acids. For employment in comparative experiments the nickel was worked up by the procedure recommended by Covert and Adkins (*J. Amer. Chem. Soc.*, 1932, **54**, 416) for the production of a specially active catalyst. Since the product ignited spontaneously when allowed to dry in air, it was preserved under alcohol: as a result, the small portions of catalyst required in the different experiments could not expeditiously be weighed out with precision, and in practice the proportion of catalyst taken (usually 0.5 g. per 10 g. of sorbic acid) was determined only approximately. When shaken with hydrogen, the catalyst absorbed an appreciable amount of the gas (30 c.c. per 0.5 g.), so it was always necessary in quantitative experiments to treat the catalyst with hydrogen before actually employing it for reduction. The active nickel prepared by the procedure of Covert and Adkins reduced sorbic acid and sodium muconate somewhat more slowly than did platinum; the less active preparations obtained by allowing the finely powdered alloy to stand in the cold with excess of caustic soda until the aluminium had dissolved promoted reaction still more slowly, for, whereas these latter preparations, in 0.5 g. portions, required about 7.75 hours for the reduction of 5.6 g. of sorbic acid, the more active preparation required only 1.75 hours. The partial hydrogenation products were freed from catalyst and solvent as previously described.

Expt. 1. The nickel catalyst employed in this preliminary experiment was less active than that used in all succeeding experiments; furthermore, the nominal degree of hydrogenation (50%) was not quite attained, since the necessity for a preliminary treatment of the catalyst with hydrogen had not been realised. The hydrogenation product from 5.6 g. of sorbic acid yielded, when slowly distilled under reduced pressure, (a) a distillate (4.51 g.) which partly solidified at room temperature, and (b) a residue which when partly distilled from a small vessel gave a semi-solid distillate (0.62 g.) free from sorbic acid, leaving a solid residue (0.47 g.). The latter residue when fractionally crystallised from petroleum (b. p. 60—80°) yielded impure sorbic acid (0.3 g.) and Δ^{α} -hexenoic acid (0.1 g.). The two semi-solid distillates (total weight, 5.13 g.), which consisted mainly of Δ^{α} -hexenoic acid, were combined and recrystallised several times from petroleum: there were ultimately obtained pure Δ^{α} -hexenoic acid (3.18 g.) and a liquid which was separable on partial esterification with alcoholic hydrogen chloride (see this vol., p. 306) into an acidic material (0.76 g.), consisting entirely of Δ^{α} -hexenoic acid so far as could be determined, and a neutral ester (1.0 g.). The total amount of Δ^{α} -hexenoic acid was thus approximately 3.94 g. (70% yield), and that of recovered sorbic acid 0.30 g. (5.4% yield).

Expt. 2. The 50% hydrogenation product from 5.6 g. of sorbic acid largely solidified on cooling. By partial recrystallisation from light petroleum, pure Δ^{α} -hexenoic acid (3.6 g.) was obtained, together with a liquid residue which yielded on partial esterification with alcoholic hydrogen chloride solid Δ^{α} -hexenoic acid (1.25 g.) and a (crude) neutral ester (0.75 g.). Thus the total amount of Δ^{α} -hexenoic acid isolated was 4.85 g. (86%). The neutral ester, on oxidation at 0° with permanganate, yielded calcium oxalate equivalent to 0.21 g. of Δ^{α} -hexenoic acid and a very small quantity of succinic acid, which was identified by comparison with an authentic specimen. No unchanged sorbic acid was isolated, but possibly the failure to detect a very

small proportion thereof was due to the omission in this experiment of the customary series of partial distillations.

Expt. 3. A careful repetition of the preceding experiment employing 11.2 g. of sorbic acid and reverting to the distillation procedure for separating unchanged sorbic acid yielded (a) a liquid fraction (2.54 g.), (b) a solid fraction consisting of pure Δ^{α} -hexenoic acid (7.2 g.), and (c) a residue which on fractional crystallisation from petroleum (b. p. 60—80°) yielded impure sorbic acid (0.37 g.), Δ^{α} -hexenoic acid (0.5 g.), and a residue (0.47 g.) which contained some hexenoic acid and some sorbic acid. The liquid fraction (a), on partial esterification with alcoholic hydrogen chloride, yielded a further quantity of Δ^{α} -hexenoic acid (1.66 g.) and 1 g. of (crude) neutral ester. The latter, containing the saturated hydrogenation product (esterified), decolorised only 35 c.c. of 3.2% permanganate when treated with this reagent at 0°: this degree of unsaturation corresponded to a probable approximate content of 0.4 g. of ethyl hexoate and 0.6 g. of ethyl hexenoate (Δ^{β} - or Δ^{γ} -). From the oxidation product, 0.05 g. of impure succinic acid was isolated (identified after purification by comparison with an authentic specimen), some calcium oxalate, and a little (unidentified) fatty acid. The hydrogenation product contained, therefore, at least 83% of Δ^{α} -hexenoic acid, a little Δ^{γ} -hexenoic acid (about 0.4%), possibly a little Δ^{β} -hexenoic acid, although the presence of this substance was not actually demonstrated, some hexoic acid, and an amount of unchanged sorbic acid equivalent to the hexoic acid.

Partial Hydrogenation of Sodium Muconate in Water.—50% Hydrogenation in presence of activated nickel was carried out as previously described for platinum (this vol., p. 307). The aqueous product, after removal of the catalyst, was freed directly from the bulk of unchanged muconic acid by careful acidification* in dilute solution and filtration. The acidic residue derived by evaporation of the filtrate was directly submitted to partial esterification with methyl-alcoholic hydrogen chloride, whereby a mixture of neutral and acidic esters, together with a further very small quantity of muconic acid, was obtained. From the respective amounts of (a) methyl hydrogen *trans*- Δ^{α} -dihydromuconate (m. p. 60°), (b) unchanged muconic acid, (c) methyl $\beta\beta'$ -dibromoadipate,† and (d) methyl adipate derived from the reduction product (see this vol., p. 307) in several consecutive experiments, the relative degrees of non-hydrogenation, dihydrogenation ($\alpha\beta$ - and $\alpha\alpha'$ -), and tetrahydrogenation shown on p. 1932 were calculated. The description and proof of structure of the methyl hydrogen Δ^{α} -dihydromuconate, m. p. 60° (previously reported m. p. 58°), obtained in these and former experiments and subsequently obtained by equilibration of Δ^{β} -dihydromuconic acid with caustic soda, followed by partial esterification, are given in the succeeding paper (p. 1938).

The 50% hydrogenation of methyl *cis-cis*-muconate could not be studied quantitatively owing to the serious experimental difficulties attending the separation of the components of the reduction mixtures. A description of the qualitative production and of the properties of both methyl and ethyl *cis*- Δ^{α} -dihydromuconate by partial reduction of the corresponding esters of *cis-cis*-muconic acid is included in the succeeding paper.

C. Hydrogenations with Palladium Catalysts.

Preparation of Catalysts.—Four varieties of palladium catalyst were employed in different experiments. These were prepared in adequate quantity for carrying out a number of experiments, and preserved in well-stoppered bottles: (1) Palladium supported on barium sulphate, prepared by the method of Schmidt (*Ber.*, 1919, 52, 409), was used in the proportion of 0.2 g. of catalyst to 5.6 g. of sorbic acid. (2) Palladium supported on calcium carbonate, prepared by the method of Busch and Stöve (*Ber.*, 1916, 49, 1064), was used in the proportion of 1 g. of catalyst to 5.6 g. of sorbic acid. (3) Palladous oxide, PdO, prepared by the method of Adams and Shriner (*J. Amer. Chem. Soc.*, 1924, 46, 1685), was used as a source of unsupported palladium. This oxide, like platinum oxide, was reduced to the metallic state in the reaction vessel by shaking with hydrogen, and was used in the proportion of 0.1 g. to 5.10 g. of conjugated acid. (4) Platinised active charcoal (consisting of 10% of platinum and 90% of a sugar charcoal designated "Suchar," prepared by Imperial Chemical Industries Ltd.) on which palladium from palladium chloride solution (1.6 c.c. of 10% solution per g. of platinised charcoal) had been

* Any considerable excess of mineral acid increases the difficulty of separating the products completely owing to lactonisation of the Δ^{α} -acid.

† This bromide did not consist wholly of the high-melting form, so the percentage figure for the Δ^{β} -acid was based on the total weight of (di)bromide obtained from the (esterified) residue of the reduction product left after separation of unchanged conjugated and Δ^{α} -dihydro-acid.

deposited according to the method of Zelinsky, Packendorff, and Leder-Packendorff (*Ber.*, 1933, 66, 872) was used in the proportion of 0.25 g. of catalyst to 5.6 g. of sorbic acid.

50% *Hydrogenation of Sorbic Acid*.—A series of reductions (each repeated at least once) was carried out, using in the respective cases the four catalysts mentioned above. Prior to each reduction the catalyst specimen employed was shaken with hydrogen until no more gas was absorbed. The reduction product was in each case freed from catalyst and worked up as follows. First it was fractionally distilled, the highest-boiling (undistilled) portion being carefully examined for sorbic acid by fractional crystallisation from light petroleum; then the distillate, crystallising in the receiver and obviously consisting mainly of Δ^{α} -hexenoic acid, was partially esterified and so separated into a major portion of (unesterified) crystalline Δ^{α} -hexenoic acid and a minor portion of crude oily ester derived from the Δ^{γ} -, Δ^{β} -, and a little of the (unavoidably esterified) Δ^{α} -hexenoic acid present in the reduction mixture. In the case of palladium-calcium carbonate a small proportion of sorbic acid was isolated and the approximately equivalent proportion of hexoic acid shown to be present; also in the case of the palladium catalyst derived from palladium oxide a very small proportion of sorbic acid was recovered unchanged. The crude ester was oxidised at 0° with 3% permanganate, and the proportions of the Δ^{α} - and Δ^{γ} -esters contained therein deduced from the proportions of oxalic and succinic acids produced.

A typical case is that of the 50% reduction of sorbic acid (in quantities from 5.8 g. to 40.7 g.) by the aid of palladium-calcium carbonate. Nearly the whole of the reduction product distilled at 119—120°/20 mm., the major part solidifying in the condenser, leaving a solidifiable residue in the flask, from which a little sorbic acid was isolated by crystallisation from light petroleum. The whole of the distillate and the low-melting portion of the residue were submitted to partial esterification, the latter, together with the highest-boiling portion of the distillate, being treated separately in order to facilitate the complete separation of (unesterified) sorbic acid. In this way sorbic acid (maximum total yield, 3.6%), solid Δ^{α} -hexenoic acid, and a mixture of esters were separated, the last two being finally distilled once without the use of a column. The odour of the mixture of esters in this example indicated that some hexoic ester was present. The degree of unsaturation was experimentally determined by the hydrogenation of samples of the mixture and hence the proportion of fully saturated material was ascertained. This, as theory required, corresponded reasonably closely with the percentage of unchanged sorbic acid actually recovered. The bulk of the ester mixture (b. p. 69°/20 mm.) was oxidised with cold alkaline permanganate, the process being continued at room temperature as far as possible: allowing, however, for the proportion of hexoic ester known to be present, the theoretical quantity of permanganate was not reduced, indicating the presence of some material which resisted complete oxidation under these conditions. The oxidation product contained succinic acid and a little oxalic acid, from the proportions of which, respectively, the percentage yields of Δ^{γ} - and residual (unavoidably esterified) Δ^{α} -acid were calculated.* The succinic acid was isolated as such from the oxidation product after the oxalic acid had been removed by precipitation as calcium oxalate in the presence of dilute acetic acid. The oxalic acid was estimated volumetrically. Since the oxidation was not quite complete, a syrupy acidic residue remaining which, although doubtless partly composed of hexoic acid, yielded a little more succinic acid but no oxalic acid on further treatment with permanganate, another estimate of the succinic acid produced was made by oxidising a fresh quantity of a 50% reduction product of sorbic acid directly with permanganate without previous separation of the bulk of the Δ^{α} -acid; a somewhat higher percentage figure was thereby obtained.

In all reductions there was a discrepancy between the sum of the yields of Δ^{γ} -, residual Δ^{α} -hexenoic, and hexoic (when present) esters and the total yield of mixed esters. This is attributed to the presence of Δ^{β} -hexenoic ester, but no satisfactory means of estimating the latter was discovered; in the case of the palladium-calcium carbonate reduction product, however, an attempt was made to achieve partial separation of propionic acid, arising by degradation of the Δ^{β} -acid, from the acetic and butyric acids arising from the Δ^{γ} - and Δ^{α} -acids respectively. The mixture of acids was extracted with ether from the (acidified) permanganate oxidation product, after the oxalic acid present therein had been precipitated as the calcium salt in alkaline solution, and the filtrate concentrated: the extract was dried, and the fatty acid isolated therefrom (in rather poor yield) fractionated as adequately as possible in a small apparatus. The middle fraction (b. p. 135—145°) was converted into the corresponding *p*-toluidide, the

* The possibility that traces of oxalic acid may arise by oxidation of Δ^{β} -hexenoic acid is discounted by the fact that mixtures of Δ^{β} - and Δ^{γ} -hexenoic acid produced by "nascent" reduction of sorbic acid yield no oxalic acid with permanganate if carefully freed from unchanged sorbic acid.

non-homogeneous derivative being boiled with petroleum (b. p. 60—80°) to extract material of low melting point (apparently containing the *p*-toluidide of butyric acid, m. p. 75°), and the residue then fractionally crystallised from benzene. Although no adequate separation of the individual *p*-toluidides present could be effected, a considerable fraction of m. p. 117—120° was obtained which appeared to consist mainly of the *p*-toluidide of propionic acid, since on admixture with an authentic specimen of the latter (m. p. 126°) it melted at 118—122°, but on admixture with the *p*-toluidide of acetic acid (m. p. 153°) it melted at 95—110°. An attempt to obtain a purer derivative of the propionic acid produced by oxidation, by conversion of the crude fatty acid into the corresponding monochloro-derivative, and thence into the corresponding malonic acid, failed, since the mixture of malonic acids produced proved to be more difficult of resolution than the above-mentioned *p*-toluidides.

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