CCXV.—*Properties of Conjugated Compounds. Part V. The Hydrogenation of Certain Extended Heterogeneous Systems.*

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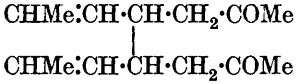
THE literature bearing on hydrogen addition to conjugated compounds containing simple butadienoid, extended or heterogeneous systems indicates an overwhelming and apparently exclusive tendency to the $\alpha\delta$-attachment of hydrogen. Observations on the attachment of other addenda (see the previous papers of this series) render it certain that, although terminal products may frequently arise in the hydrogenation process, they cannot be the exclusive *primary* products of addition, unless (*a*) propenoid activity is absent as a feature of the hydrogenation process under all conditions, or (*b*) the position of equilibrium connecting alternative propenoid forms (as determined by the groups attached to the three-carbon chain) favours under all conditions of hydrogenation, excluding catalytic processes, the formation of terminal products. Experiments on the hydrogenation of different varieties of conjugated compounds have shown that terminal addition of hydrogen is not universal, and the hydrogenation of certain heterogeneous substituted butadienes will now be described.

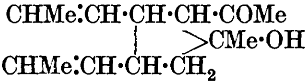
It has been recorded by one of us (J., 1923, **123**, 2531, *et seq.*) that muconic acid, its esters and its $\alpha\alpha'$-dihalogenated (substituted) derivatives are converted by hydrogenation into Δ^{β}-dihydrocompounds. In all the experiments with these substances the most painstaking search has failed to reveal the presence of any trace of a Δ^{α}-compound. To the methods previously employed, in which the reducing medium was strongly acid or alkaline, is now added that of reduction in neutral solution by means of aluminium amalgam. Ethyl muconate may be hydrogenated quite readily in this way, but the sole product is again the Δ^{β}-compound. One of the objects of this prolonged series of reductions in the muconic group is to establish beyond doubt that the muconic system, as representing a butadiene chain symmetrically substituted by carbonyl, yields exclusively (so far as separative methods indicate), with hydrogen generated in the usual different ways, a product hydrogenated at the $\alpha\delta$-carbon atoms. It has been sought to compare the hydrogenation product of the analogous, but unbalanced, heterogeneous compound $\mathrm{CH_3{\cdot}CO{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H}$ with that of muconic acid : up to the present, however, the synthesis of this ketonic acid in adequate quantities has resisted our efforts. The butadiene monocarboxylic acids and ketones, on the other hand, are readily prepared in quantity, and the differentiation to be anticipated on polar grounds between their hydrogenated products and those of muconic derivatives is found in practice.

Hydrogenation of crotylideneacetone ($\mathrm{CHMe{:}CH{\cdot}CH{:}CH{\cdot}COMe}$) in moist ethereal solution by aluminium amalgam yielded upwards of 80% of a compound derived from two molecules of the ketone. This substance, doubtless a cyclised form of the diketone (I), absorbed four atoms of hydrogen when catalytically hydrogenated, and yielded by ozone oxidation acetaldehyde together with an aldehydic oil : the latter, not satisfactorily oxidisable with permanganate, yielded succinic acid when heated with a solution of chromic acid.

(I.)



$$\begin{array}{l} \mathrm{CHMe{:}CH{\cdot}CH{\cdot}CH_2{\cdot}COMe} \\ \qquad\qquad\quad | \\ \mathrm{CHMe{:}CH{\cdot}CH{\cdot}CH_2{\cdot}COMe} \end{array}$$



$$\begin{array}{l} \mathrm{CHMe{:}CH{\cdot}CH{\cdot}CH{\cdot}COMe} \\ \qquad\qquad\quad | \qquad > \mathrm{CMe{\cdot}OH} \\ \mathrm{CHMe{:}CH{\cdot}CH{\cdot}CH_2} \end{array}$$

(II.)

To this main reduction product, closely resembling the bimolecular reduction products of mesityl oxide and phorone, the formula (II) is assigned (although the very great resistance of the mesityl oxide product in particular towards permanganate, and its oxidation by chromic acid to a succinic acid—not to a glutaric acid—are somewhat remarkable features for a compound of the monocyclic structure assigned). The bulk of the residual reduction product consisted of an unsaturated, pinacol-like compound also derived from two molecules of the ketone : its constitution is uncertain. Simple dihydro-ketones were absent, or present only in very small proportion.

Sorbic acid yielded, when reduced in moist ethereal solution with aluminium amalgam, a mixture of Δ^{β}- and Δ^{γ}-dihydrosorbic acids ($CH_2Me{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H$ and $CHMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, respectively). A similar mixture was produced by reduction by the action of (*a*) aluminium amalgam on an aqueous neutral solution of sodium sorbate, (*b*) sodium amalgam on a glacial acetic acid solution of sorbic acid, and (*c*) sodium amalgam on an aqueous solution of sodium sorbate through which carbon dioxide was being passed. We are indebted for the observation (*c*) to Mr. Goldberg, who first observed, while endeavouring to obtain pure Δ^{β}-dihydrosorbic acid by a slight modification of Fittig's sodium-amalgam method, that a reduction product of sorbic acid yielded acetaldehyde on ozonisation and therefore could not be the homogeneous Δ^{β}-acid. An approximate estimate (representing a lower limit) of the Δ^{γ}-acid in these acid mixtures was made by estimating the succinic acid derived by permanganate oxidation in neutral solution. Under the conditions of the first three of the above-mentioned methods of reduction the proportions of the Δ^{γ}-acid were approximately 35, 40, and 30%, respectively. The oxidation fragment complementary to succinic acid—acetic acid—was recognisable, although mixed with propionic acid arising from the Δ^{β}-acid; the malonic acid theoretically derivable from the Δ^{β}-acid had, however, been entirely converted into acetic acid.

Although the orientation of the hydrogenation products of sorbic acid appears very similar under the different experimental conditions, it is possible that in other instances the mode of generating hydrogen (as distinct from the capacity of the medium to bring about a $\alpha\beta$–$\beta\gamma$ change after the addition; compare the recent reduction of cinnamylidenefluorene by Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 123, in which the 1 : 4- is converted into the 3 : 4-dihydro-compound in akaline solution) has an effect on the orientation of the reduction products. Such a differential effect might be a reflexion, wholly or partly, of differences in the condition of the attacking hydrogen. Whether this be so or no, a major influence on the orientation of the products would seem to be that of the groups attached to the original butadiene system, as exemplified by the four isomeric methylbutadiene-α-carboxylic acids and the three toluic acids, some of which are at present being examined.

EXPERIMENTAL.

Hydrogenation of Ethyl Muconate in a Neutral Medium.—Ethyl muconate (28 g.), dissolved in moist ether, was left in contact with amalgamated aluminium foil for 16 hours. The ester obtained from the filtered product (24 g.) distilled at 127°/12 mm., leaving a small residue, and was pure ethyl Δ^{β}-dihydromuconate, homogeneity being established by the tests: (i) careful oxidation with dilute neutral permanganate at 0° yielded no succinic acid; (ii) the amide formed almost quantitatively with concentrated aqueous ammonia was the homogeneous amide of the Δ^{β}-ester (m. p. 212—214°); (iii) the acid derived by rapid hydrolysis with hydrochloric or dilute sulphuric acid was found on careful fractional crystallisation to consist only of Δ^{β}-dihydromuconic acid, m. p. 195°.

Hydrogenation of Crotylideneacetone.—The ketone (Meerwein, *Annalen*, 1908, **358**, 85) (40 g.) was dissolved in moist ether and left in contact with amalgamated aluminium foil for 16 hours. Filtration of the product and evaporation of the solvent yielded a colourless oil, from which four fractions were obtained: (i) 1—1½ g., b. p. below 80°/19 mm.; (ii) 2—3 g., b. p. 80—158°/19 mm.; (iii) 18 g., b. p. 158—168°/17 mm.; (iv) 8 g., b. p. 168—178°/17 mm. Fractions (iii) and (iv) were separately submitted to steam distillation: almost the whole of the former and the major portion of the latter distilled. The non-volatile material remaining in the mother-liquors was obtained, on extraction, as a very viscid liquid (2 g.), b. p. 175—180°/16 mm.: it possessed some of the characteristics of an unsaturated pinacol, but its exact constitution was not determined. The combined aqueous distillates yielded a colourless, somewhat viscid liquid (b. p. 169—178°/23 mm.) which absorbed hydrogen readily (4 atoms per molecule on the formula assigned) when reduced catalytically, and arose apparently in strictly analogous fashion to the bimolecular reduction products of mesityl oxide and phorone. In view of its degradation products it is regarded as *5-acetyl-*1*-methyl-*3 : *4-dipropenyl*cyclo*pentan-*1*-ol* (II) (Found: C, 75·3; H, 9·6. $C_{14}H_{22}O_2$ requires C, 75·7; H, 9·9%). An examination of the low-boiling portion of the reduction product (about 3 g.) derived from fractions (i) and (ii) showed it to be non-ketonic: it probably consisted of methylbutadienylcarbinol, but this constitution has not been confirmed.

*Oxidation of Acetylmethyldipropenyl*cyclo*pentanol.*—The substance (2 g.), dissolved in chloroform (30 c.c.), was submitted to ozonisation for 6 hours. Removal of the solvent at reduced pressure yielded a pale yellow viscous ozonide, which was decomposed by gentle heating with water (30 c.c.). The vapours evolved during the decomposition were passed into aqueous *p*-nitrophenylhydrazine hydrochloride, with which they yielded a bulky crystalline precipitate of acetaldehyde-*p*-nitrophenylhydrazone (m. p. 126° after recrystallisation from aqueous alcohol; mixed m. p. with authentic specimen, 126°). The aqueous liquor contained an oily aldehydic product which yielded a syrupy acid when cautiously oxidised with dilute permanganate at 0°. This acid, the homogeneity of which was doubtful, was not further investigated. Since regulated oxidation of the *cyclo*pentanolones derived from 1 : 4-diketones appears rarely to be successful, the customary drastic reagent (chromic acid) for *cyclo*pentanolone degradation was employed. A cyclic aldehyde derived by ozonisation of a substance of formula (II) should yield succinic acid on oxidation with chromic acid.

Accordingly the ketone (10 g.), dissolved in glacial acetic acid (60 c.c.), was ozonised for 24 hours. To the product, diluted with a further 100 c.c. of acetic acid, a solution of chromic acid (100 g.) in 50% aqueous acetic acid (160 c.c.) was gradually added. The reaction, which at first required moderating by cooling, was completed by gently refluxing the mixture for 1 hour. Chromium was then removed from the cooled oxidation mixture by addition of alkali and filtration. The filtrate was evaporated to dryness, and the residue, after being acidified and again evaporated, was finely powdered and extracted with acetone. The extract gave a considerable amount of succinic acid.

A compound of formula (II) should give rise, by the degradation of a diozonide, to two molecules of acetaldehyde, or on oxidation with permanganate to two molecules of acetic acid. Attempts to estimate the acetic acid produced by degradation were made, but although considerable quantities of the crude acid were obtained, the presence of volatile acidic impurities rendered the figures valueless.

Hydrogenation of Sorbic Acid.—(a) *By aluminium amalgam in a neutral medium.* Amalgamated aluminium foil was allowed to react for 24 hours with a solution of sorbic acid in a large volume of moist ether. The filtered solution was washed once with water, dried, and evaporated. The oily residue was dissolved in light petroleum, and the solution twice cooled to −25° and decanted. Some unchanged sorbic acid was thus separated. After removal of the solvent the residual oily acid distilled at 96—98°/12 mm., leaving a trace of sorbic acid and a quantity of viscous liquid (possibly a bimolecular reduction product). The oily acid, which was obtained in good yield, did not solidify when cooled to −25° and its boiling point did not change on redistillation. It consisted of a mixture of Δ^{β}- and Δ^{γ}-dihydrosorbic acids as shown by oxidation (Found : C, 63·2; H, 8·6. Calc. for $C_6H_{10}O_2$: C, 63·2; H, 8·8%).

(b) *By sodium amalgam in an acid medium.* To a solution of sorbic acid (25 g.) in excess of glacial acetic acid, 3% sodium amalgam was added in small portions during 7 hours. A large volume of water was added, the mercury separated, and the solution thoroughly extracted with ether. The ethereal solution was washed several times with water, the ether evaporated, and the bulk of the residual acetic acid distilled at ordinary pressure through a short column. The residue was dissolved in petroleum, freed from unchanged sorbic acid as in (a), and distilled at reduced pressure. An oily acid (b. p. 102—103°/16 mm.) was obtained which did not solidify at —25° and was indistinguishable from the acid mixture obtained in (a). This also was a mixture of Δ^β- and Δ^γ-dihydrosorbic acids [Found: C, 63·4; H, 8·4; *M* (dibasic), 115. Calc. for $C_6H_{10}O_2$: C, 63·2; H, 8·8%; *M*, 114].

(c) *By aluminium amalgam and sodium sorbate.* Amalgamated aluminium foil was allowed to react with a neutral, aqueous solution of sodium sorbate for 24 hours. The resulting liquor was filtered, acidified, and extracted with ether. Again an oily acid (b. p. 96—98°/12 mm.), indistinguishable from the mixtures of Δ^β- and Δ^γ-dihydrosorbic acids previously obtained, resulted.

Oxidation of Mixtures of Dihydrosorbic Acids.—Specimens of each of the three mixtures obtained as above were oxidised with 3% permanganate in neutral solution. It was desired to estimate the succinic acid produced and obtain an approximation to the proportion of the Δ^γ-acid in the acid mixture.

The acid, suspended in much water, was cooled to 0° and vigorously stirred. An amount of permanganate corresponding to 4 atoms of oxygen per molecule of dihydrosorbic acid was gradually added. The product was worked up in the usual way (the manganese mud being thoroughly extracted with water), and the aqueous liquor concentrated to small bulk on a steam-bath. The product was acidified with the calculated quantity of hydrochloric acid and thoroughly extracted with ether. The mother-liquor was evaporated at room temperature in an evacuated desiccator, and the solid residue repeatedly extracted with acetone. The ethereal extract, evaporated under a long column, yielded a mixture of solid and liquid acids, the acetone extract almost entirely a solid acid. The solid acid from each extract was succinic acid: malonic acid, which should arise from Δ^β-dihydrosorbic acid, had been entirely converted into acetic acid. The liquid portion of each oxidation product was distilled: after removal of the low-boiling material, the first fraction was collected up to 120°, the second at 120—135°, and the last few drops of distillate separately; some succinic acid remained in the flask.

A portion of the first fraction was converted into its *p*-bromophenacyl ester (Judefind and Reid, *J. Amer. Chem. Soc.*, 1920, **42**, 1047), which, after recrystallisation until its melting point was constant, was found to be pure *p*-bromophenacyl acetate (m. p. 84°; mixed m. p. with authentic specimen, 84°). The last fraction similarly yielded the *p*-bromophenacyl ester of propionic acid, which after recrystallisation melted at 57—58° (mixed m. p., 58°). The yields of succinic acid obtained by the three methods of reduction correspond to the following proportions of Δ^{γ}-dihydrosorbic acid in the hydrogenated product: (a) 35%; (b) 40%; (c) 30%.

The authors desire to express their indebtedness to the Chemical Society for a grant (to J. T. E.) which has defrayed a portion of the cost of this investigation.

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[*Received, March* 22*nd*, 1928.]