LXXIV.—*Properties of Conjugated Compounds. Part IX. The Formation of Bimolecular Reduction Products of Butadiene Acids.*

By CHARLES MILLS CAWLEY, JOHN TREVOR EVANS, and ERNEST HAROLD FARMER.

EVANS and FARMER (J., 1928, 1644) have shown that the addition of hydrogen to conjugated carbon compounds is not invariably terminal, thus taking the first step towards bringing hydrogen into line with other common addenda. It has now been found that the presence of alkyl groups at different positions in the butadiene chain of β-vinylacrylic acid seems to affect the relative extents to which αβ- and αδ-dihydrogen derivatives are produced : the crudeness of the method of estimating the proportion of the αβ-acid * (Evans and Farmer, *loc. cit.*), however, prevents any confident application of the results to quantitative discrimination between alkylation effects. It has also been found in experiments with different types of butadiene compound, hydrogenated by the action of different metals, media, etc., that the formation of hydrogenated bimolecular compounds is so common that it must be considered a normal feature of reduction. Since the bimolecular compounds are frequently formed side by side with the simple dihydrogen derivatives, their theoretical significance cannot be neglected in a consideration of the mechanism of hydrogen addition.

It has been shown that linkage of monohydrogenated molecules may occur at the β-carbon atom of the butadiene chain. Corresponding linkage of reactant molecules might be expected also to be possible at the δ- or the ζ-carbon atom and the principle entailed would merely represent an extension of that underlying the formation of pinacols and the bimolecular reduction products of mesityl oxide, ethyl α-cyano-ββ-dimethylacrylate, etc.

Crotylideneacetone and ethyl crotylidenemalonate were the first instances discovered in which there was a definite departure from the rule respecting terminal hydrogen addition. The reduction products from the former of these have already been described, but the constitutions attributed at the same time to those from the

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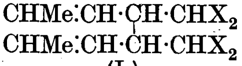
* The method presents two unsatisfactory features : (1) The acid mixture must be fractionated so thoroughly that no unreduced acid is left behind. It is well-nigh impossible to do this without sacrificing a portion of the distillate and so running the risk of changing the proportion of the isomerides. (2) In addition to the expected acids the permanganate oxidation product yields syrupy residues which survive re-oxidation processes. These are persistently obtained from the alkylsorbic acids.

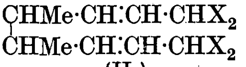
latter proved so difficult of establishment that an account of the reduction is only now possible.

The unimolecular hydrogenation products from ethyl crotylidenemalonate appear in quite insignificant quantity when aluminium amalgam is the reducing agent; almost the entire product consists of a mixture of two isomeric bimolecular *esters*, one of which is a solid. It was expected that each of these substances would be correctly represented by one or other of the formulæ (I) and (II).



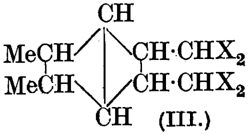
$$\begin{array}{l}\mathrm{CHMe{:}CH{\cdot}CH{\cdot}CHX_2}\\ \mathrm{CHMe{:}CH{\cdot}CH{\cdot}CHX_2}\end{array}$$

(I.)



$$\begin{array}{l}\mathrm{CHMe{\cdot}CH{:}CH{\cdot}CHX_2}\\ \mathrm{CHMe{\cdot}CH{:}CH{\cdot}CHX_2}\end{array}$$

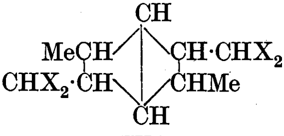
(II.)



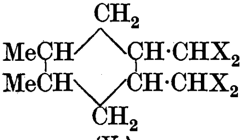
(III.)

($X = CO_2Et$)

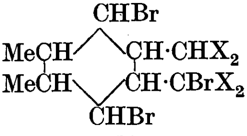
Although the composition of the substances corresponded with this expectation, it soon became obvious that both representations were incorrect. In the first place, both substances were so saturated that they were quite unaffected by permanganate at 20° or by ozone; in the second place, both substances took up two, *and only two*, atoms of hydrogen in the presence of palladium, the hydrogenation being effected with difficulty. The first of these properties could conceivably be the result of steric hindrance, but the two in combination suggested at once the dicyclic constitution (III) for the original compounds (alternatively, but improbably, IV, for one or both) and the monocyclic constitution (V) for their fully reduced derivatives. It was remarkable that with one exception all the numerous derivatives prepared from the bimolecular compounds were liquids.



(IV.)



(V.)

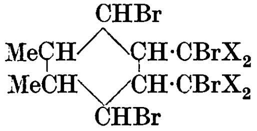


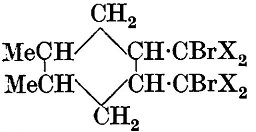
(VI.)

($X = CO_2Et$)

In the detailed examination chief attention was paid to the solid compound. This substance absorbed 4 atoms of bromine per molecule to yield a *tribromide* and 6 atoms of bromine (the limit of absorption) to yield a *tetrabromide*. The bromination process was obviously one of combined substitution and addition so that the results corresponded with the formation of (VI) and (VII) from (III). The corresponding fully reduced ester absorbed, in accordance with formula (V), only 4 atoms of bromine per molecule to yield a *dibromide* representable by (VIII). Attempts were made to oxidise to carboxyl the bromomalonic groups in the compounds to which formulæ (VII) and (VIII) apply, but oxidation always proceeded irregularly and failed to yield homogeneous products.

(VII.)

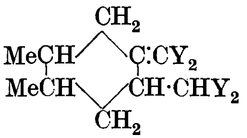




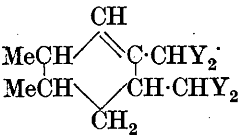
(VIII.)

($X = CO_2Et$)

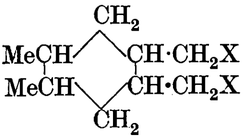
The solid bimolecular ester, when hydrolysed with alkali, yielded a mixture of unsaturated tetrabasic acids—liquid and solid : these appeared from their behaviour with permanganate to be representable by (IX) and (X) respectively. The sodium salts of this acid mixture, when reduced catalytically, yielded a somewhat impure tetrabasic acid, and this, by decarboxylation, a crude dibasic acid the ethyl ester of which agreed in composition with formula (XI). An apparently identical dibasic acid was obtained by hydrolysing and decarboxylating the fully reduced ester (V). If the bimolecular esters were representable by formula (I) or (II), the corresponding saturated dibasic acid would be dipropyladipic or dimethylsuberic acid—acids almost certainly of highly crystalline character.



(IX.)



(X.)



(XI.)

($X = CO_2Et$; $Y = CO_2H$)

Although the general behaviour of the solid bimolecular ester corresponded with the constitution (III), it was desired to gain direct evidence of the existence of an intermolecular bridge-bond at the δ-carbon atoms of the original butadiene chains. Since regulated oxidation was out of the question, various drastic oxidising agents were tried. With only one of these, hot chromic acid, was there success. This reagent broke down the solid ester to volatile acids and carbon dioxide to the extent of about 96%, but yielded a small quantity of *s*-dimethylsuccinic acid. This acid always appeared if the conditions of oxidation were not greatly changed, but the yield could not be increased.

Most of the experiments carried out with the solid bimolecular ester were also repeated with the isomeric liquid ester. No essential difference in structure between the two compounds (such, for instance, as that holding between III and IV) is adjudged to exist. Probably the two substances are geometrical isomerides, but conditions for oxidising the liquid isomeride to dimethylsuccinic acid were not discovered : under moderately drastic conditions of operation, complete degradation to volatile products ensued.

In the formation of a "para"-bridged *cyclo*hexane derivative from ethyl crotylidenemalonate, the important features from the point of view of additive mechanism are doubtless the attachment of hydrogen at the α-carbon atoms and the union of the radicals so formed at the β-carbon atoms. The subsequent establishment of bonds between γ- and δ-carbon atoms respectively may be regarded as involving an intramolecular variation of the truxillic acid condensation. Therefore, so far as these examples are concerned, true attachment of hydrogenated radicals at the δ-carbon atoms remains to be sought.

Ethyl crotylidenecyanoacetate (two forms) has also been reduced : the product consisted mainly of a bimolecular substance very similar in general properties to that from ethyl crotylidenemalonate. Owing to its high boiling point, however, adequate fractionation could not be carried out and detailed examination was abandoned.

The simple butadiene acids which have been reduced—β-vinylacrylic, sorbic, α-methylsorbic, and βγ-dimethylsorbic acids—all give considerable yields of high-boiling products which are undoubtedly bimolecular compounds; cinnamylideneacetic acid also gives an intractable acid mixture very different from the dihydrogenated product obtainable with sodium amalgam. It is hoped later to report in detail on some of these substances.

It might be supposed that constitutive influences in the conjugated compound would determine or seriously affect the formation of bimolecular reduction products as well as that of simple αβ- and αδ-dihydrogen derivatives. Actually, however, the character of the metal and medium employed in reduction appears to exercise a more important influence. Evans and Farmer looked for a difference in the proportion of αβ- and αδ-dihydrogen derivatives of sorbic and β-vinylacrylic acids to be obtained by using different metals, and media of different acidity (alkalinity), but since the experimental figure for the αβ-acid in each case could only be regarded as a lower limit of production, no definite conclusion was possible. Shortly afterwards, however, the appearance of Willstätter, Seitz, and Bumm's paper on the reduction of terephthalic, $\Delta^{1:3}$-dihydroterephthalic and Δ^{2}-tetrahydroterephthalic acids (*Ber.*, 1928, **61**, 871) made plain that the character of the reduction product from the first of these is determined by the hydrogen-ion concentration of the medium and that with pure sodium amalgam, under carefully controlled conditions of alkalinity, the last of these may be reduced *more readily* than the corresponding Δ^{1}-acid. Burton and

Ingold (J., 1928, 904) have now recorded figures representing the comparative extents to which the αβ-dihydrogen derivatives of sorbic and vinylacrylic acids are formed by sodium in a weakly alkaline and in a weakly acidic medium, but the effect of different metals remains undetermined. From such comparative experiments as have been made by the authors, aluminium amalgam in an aqueous medium appears specially prone to yield bimolecular compounds and all the compounds referred to above can be obtained through its agency. Since a similar state of affairs holds in the reduction of ethylenic acids and ketones by metals, the attribution of reductive polymerisation to a primarily constitutive cause would appear to be ruled out, and consequently the αβ, βγ-ratio of simple dihydrogenated molecules (primarily dependent on constitution so far as experiments have yet shown) would seem in all probability to be unaffected by the concurrent formation of bimolecular compounds.

The hydrogenation mechanism suggested by Ingold in discussing the results of Evans and Farmer (*Chem. and Ind.*, 1928, **47**, 268) would allow for this probability, but the theoretical basis of the hydrogenation hypothesis subsequently developed (Burton and Ingold, J., 1928, 904; 1929, 2022) appears insufficiently broad to cover Willstätter, Seitz, and Bumm's result with Δ^2-tetrahydroterephthalic acid. (It should be stated, however, that attempts by one of the authors to reduce in similar fashion Δ^{β}-dihydromuconic acid have so far been unsuccessful.)

EXPERIMENTAL.

Reduction of Ethyl Crotylidenemalonate.—A moist ethereal solution of the ester (prepared by the method of Meerwein, *Annalen*, 1908, **358**, 82) was allowed to react with amalgamated aluminium foil for 36 hours. The reduction product was an oil which partly solidified when strongly cooled. The solid portion crystallised from petroleum in stout prisms, m. p. 61·5° (Found : C, 61·8; H, 8·1. $C_{22}H_{34}O_8$ requires C, 62·0; H, 8·0%), and the liquid distilled as a colourless oil, b. p. 235—240°/14 mm. (Found : C, 61·5; H, 7·8%). These two substances, considered to be isomeric forms of *ethyl* 1 : 2-*dimethyl*bicyclo*hexane*-4 : 5-*dimalonate* (*ethyl butane*-$^{2:3}$II$^{1:2}$-cyclo*butane*-3 : 4-*dimalonate*) (III), represented the whole of the reduction product save a very small proportion of low-boiling material. The yield of the solid product was always about 15%.

Investigation of the Low-boiling Reduction Product.—This material, accumulated from a series of reductions, was not homogeneous. After several distillations a few grams of liquid, b. p. 133—140°/18 mm., were separated, the first fraction being rejected. Specimens of this substance were oxidised with neutral permanganate in order to find if simple $\alpha\beta$- and $\alpha\delta$-dihydrogen derivatives of ethyl crotylidenemalonate were present. Some of the material appeared to be saturated, since considerably less than the calculated quantity of permanganate was reduced. The product, which contained no recognisable trace of succinic acid, consisted of a volatile acid and a little oxalic acid. The former, treated with *p*-bromophenacyl bromide, yielded a solid derivative, which was fractionally crystallised. The *p*-bromophenacyl derivative of acetic acid, m. p. 82—83°, was thus isolated, but the corresponding derivative of propionic acid, which appeared also to be present, could not be separated in pure form. Ozonisation experiments yielded no further information.

Unsaturation of the Main Reduction Products.—Both the solid and the liquid substance which constituted the main reduction product remained inappreciably attacked when vigorously shaken with aqueous permanganate at room temperature or when kept in acetone solution in contact with permanganate for several days. Both substances appeared to be little changed by prolonged treatment with ozone, and, even when boiled with permanganate in acetone solution, suffered change extremely slowly. Regulated oxidation was therefore impossible.

Nevertheless, both esters became further hydrogenated when dissolved in alcohol and shaken with hydrogen in the presence of colloidal palladium. Absorption of hydrogen was at first moderately rapid, but the rate decreased until it was barely 1 c.c. per hour. The hydrogen pressure was increased to 2 atmospheres, but still the rate of absorption was very slow. When absorption finally ceased, both esters had taken up the equivalent of two atoms of hydrogen per molecule. Both products, when isolated in the usual way, were colourless oils: that from the solid ester distilled at 225—230°/7 mm. and corresponded in composition with *ethyl* 1 : 2-*dimethylcyclohexane*-4 : 5-*dimalonate* (V) (Found : C, 61·8; H, 8·6. $C_{22}H_{36}O_8$ requires C, 61·7; H, 8·5%); that from the liquid ester distilled at 217—223°/13 mm. and was isomeric with the first (Found : C, 61·8; H, 8·2%).

The Dicyclic Reduction Products.—(1) *Hydrolysis.* The solid compound (1 mol.) was warmed with alcoholic caustic soda derived from the calculated quantity of sodium (4 atoms). The sodium salt immediately deposited was collected and dissolved in a little water, and the solution evaporated to dryness. The residue, acidified with the calculated quantity of hydrochloric acid and diluted with an equal volume of water, yielded crystals of an acid. These were filtered off and the mother-liquor was thoroughly extracted with ether. The ethereal extract yielded a syrupy acid. Some decarboxylation accompanied hydrolysis.

The solid acid (35% yield), when reprecipitated from ethereal solution by addition of petroleum, formed a crystalline powder, m. p. 175° with evolution of carbon dioxide. It was an unsaturated tetrabasic acid, which at 0° rapidly decolorised an amount of permanganate equivalent to 3 atoms of oxygen per molecule (more could be reduced slowly). The oxidation product was an enolic syrupy acid of doubtful homogeneity which could not be purified or successfully broken down to known compounds. The solid acid is probably to be represented as *1 : 2-dimethyl-*Δ^5-cyclo*hexene-4 : 5-dimalonic acid* (X) (Found : C, 53·5; H, 6·0. $C_{14}H_{18}O_8$ requires C, 53·5; H, 5·7%).

The liquid acid did not consist entirely of a tetrabasic substance. It readily lost carbon dioxide on heating, rapidly reduced cold permanganate (3 atoms of oxygen per molecule), and yielded an oxidation product somewhat similar to that derived from the solid acid, except that a proportion of oxalic acid was also formed. It probably represented a mixture of partly decarboxylated dimethyl*cyclo*hexene- and dimethyl*cyclo*hexylidene-dimalonic acids.

The liquid ester also yielded a bulky sodium salt when warmed with alcoholic caustic soda. The acid derived therefrom was wholly syrupy and could not be purified. On oxidation with permanganate the latter yielded some oxalic acid and a large proportion of syrupy acid. Numerous attempts were made to obtain solid or homogeneous liquid acids (*a*) by the decarboxylation of the tetrabasic acids described above and (*b*) by the decarboxylation of their oxidation products. All the products, however, were liquid acids of doubtful homogeneity.

(2) *Bromination.* The solid ester (chloroform solution), when treated with the equivalent of 4 atoms of bromine per molecule, yielded an oily *tribromo*-derivative (Found : Br, 36·6. $C_{22}H_{33}O_8Br_3$ requires Br, 36·1%), which solidified after long standing; when treated with the equivalent of 6 atoms of bromine, an oily *tetrabromide* was obtained which would absorb no more bromine (Found : Br, 42·6. $C_{22}H_{32}O_8Br_4$ requires Br, 43·0%). It was attempted to oxidise the bromomalonic groups of the tetrabromide to carboxyl by gradually adding finely powdered permanganate to an acetone solution of the bromide containing some free caustic alkali. Oxidation proceeded, but the product consisted of some oxalic acid and a large amount of a viscous acid which would not crystallise.

(3) *Degradation.* Since oxidising agents were almost without action on them, the dicyclic esters were subjected to vigorous oxidation with chromic acid. To the solid ester (10 g.), dissolved in glacial acetic acid (160 c.c.), a solution of chromic acid (50 g.) in 50% acetic acid (80 c.c.) was slowly added in small portions, the

mixture being continuously shaken and finally heated on a steam-bath for 1 hour. The product, from which acetic acid was removed by steam distillation, was saturated with sulphur dioxide and kept over-night; the excess of sulphur dioxide was then boiled off and the solution was made alkaline with concentrated aqueous ammonia and filtered. The filtrate, combined with several aqueous extracts of the chromium oxide, was evaporated to small bulk, acidified, and finally evaporated to dryness. The residue, when extracted with ether, gave a small yield of a slightly syrupy, solid acid. This, when drained and recrystallised from ether, formed colourless prisms, m. p. 192—193°, which were identified as *trans-s*-dimethylsuccinic acid (Found: C, 49·5; H, 6·9. Calc.: C, 49·3; H, 6·8%. Mixed m. p. with an authentic specimen, 192—193°).

Similar experiments were carried out with the liquid dicyclic ester, but the conditions for getting even a small yield of a solid degradation product were not found.

The Monocyclic Products of Complete Reduction.—(1) *Hydrolysis and decarboxylation.* In attempting to derive 1 : 2-dimethyl*cyclo*hexane-4 : 5-diacetic acid from the solid dicyclic ester, two methods were employed: (*a*) the catalytically reduced ester was hydrolysed with the theoretical quantity of alcoholic caustic soda, the derived acid being decarboxylated by heating at 180°, and (*b*) the dicyclic ester was hydrolysed with alcoholic caustic soda, the sodium salt catalytically reduced, and the derived acid decarboxylated by heating to 180°. (Re-submission of the decarboxylated acid to hydrogenation resulted in no further absorption of hydrogen.) The crude reduced tetrabasic and dibasic acids obtained in both processes were liquids which showed no tendency to crystallise. No difference was observed between corresponding products and since the second process was the more economical, a considerable quantity of the dibasic acid was thereby prepared. This was esterified with alcohol and hydrogen chloride, and the product distilled. The distillate was a colourless oil, b. p. 179°/9 mm., which is considered to be *ethyl* 1 : 2-*dimethyl*cyclo*hexane*-4 : 5-*diacetate* (Found: C, 67·45; H, 10·1. $C_{16}H_{28}O_4$ requires C, 67·55; H, 9·9%). A portion of this ester was re-hydrolysed with alcoholic caustic soda. The free acid was a colourless oil which still showed no tendency to crystallise. Since it could not be distilled, it contained traces of impurity (Found: *M*, dibasic, 237. $C_{12}H_{20}O_4$ requires *M*, 228).

(2) *Bromination and oxidation.* The fully reduced derivative of the solid dicyclic ester, dissolved in carbon disulphide, absorbed 4 atoms of bromine per molecule (with evolution of hydrogen bromide). The product, *ethyl* 1 : 2-*dimethyl*cyclo*hexane*-4 : 5-*di*-

bromodimalonate (VIII), when well washed and freed from solvent, was obtained as a yellow oil (Found : Br, 26·3. $C_{22}H_{34}O_8Br_2$ requires Br, 27·3%). This was used without further purification in an attempt to oxidise the bromomalonic groups (bromine first being replaced by hydroxyl through the action of cold caustic potash) to carboxyl. Permanganate, dissolved in acetone, was the reagent employed, but oxidation did not proceed smoothly to yield the desired dimethyl*cyclo*hexanedicarboxylic acid. As expected, oxalic acid was formed, but the accompanying gummy acid when esterified yielded an ester which was far from homogeneous.

Ethyl Crotylidenecyanoacetate.—Crotonaldehyde and ethyl cyanoacetate, mixed in molecular proportion, were cooled to −15° and a little piperidine was added. The mixture was allowed to attain room temperature and was then kept at 30° for 24 hours. There were two products : (1) a solid which crystallised from petroleum in colourless prisms, m. p. 57—58° (Found : C, 65·6; H, 6·7. $C_9H_{11}O_2N$ requires C, 65·4; H, 6·7%), and (2) an isomeric liquid, b. p. 122°/9 mm. (Found : C, 65·8; H, 6·5%).

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.
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