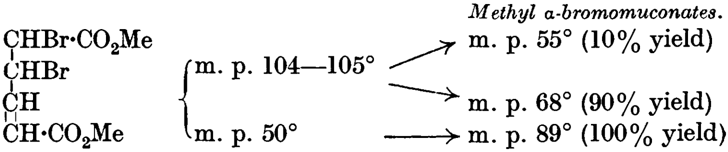
# LX.—*Muconic and Hydromuconic Acids. Part IV. Geometrical Form and Reducibility.*

By Ernest Harold Farmer and Walter Mark Duffin.

Geometrical isomerides of the muconic acid series possess a considerable degree of permanency and can be kept in the light and enter into reaction without change of geometrical form (J., 1923, **123**, 2531). The effect of geometrical form on certain types of molecular reactivity can readily be observed, therefore, and comparison be made with the behaviour of simple ethylenic compounds. In studying the hydrogenation process, twelve compounds of the muconic acid series have been submitted to reduction and every effort has been made to trace variation from the standard type of reduction product.

## I. *Monohalogenated Muconic Esters.*

When *trans-trans*-methyl muconate is treated with bromine, two stereoisomeric bromides (I) are obtained; both of these forms revert to the parent substance on treatment with zinc. On treatment with organic bases, however, each isomeride behaves differently and three monobromomuconic esters are obtained according to the scheme:

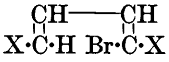


$CHBr{\cdot}CO_2Me{-}CHBr{-}CH{=}CH{\cdot}CO_2Me$

(I.)

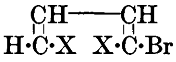
Careful search for the remaining one of the four theoretically possible isomerides (II), (III), (IV), and (V), in large quantities of material, proved fruitless. Although both the parent dibromides are *racemic* forms, the more fusible (corresponding to the racemic forms in the substituted succinic acids) might be expected to yield the less fusible (*trans-trans-*) methyl bromomuconate, and the less fusible (corresponding to a *meso*-form), the more fusible (geometrically inverted) form of methyl bromomuconate. In the absence of an absolute method of determining geometrical form, use has been made of their capacity for amide formation—a method typical of those used in observing steric effects. If, in the ester–amide transformation, activation preliminary to amide formation be assumed, it would appear to be restricted to the carbalkyloxy-groups acting as self-contained systems; otherwise, according to current conceptions of the activation process in unsaturated chains, the distinction between geometrical forms must disappear.

Each isomeride yielded an amide, two of the forms readily and without degradation, and the third with much greater difficulty and gross decomposition. Derivation, speed of amide formation and solubility being taken into account, the three isomeric methyl α-bromomuconates would seem to be capable of classification as below; since, however, in considering the main product of bromine addition to *trans-trans*-methyl muconate the method of geometrical inversion employed leads to more than one form, of which that regarded as *cis-cis* predominates, it is evident that molecular disturbance has gone too far to allow of the assumption that the *cis-trans*-form produced is necessarily that isomeride (IV) arising by simple inversion at one double bond.



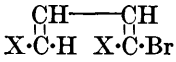
$$\begin{array}{cc} \mathrm{CH} & \!\!\text{——}\!\! & \mathrm{CH} \\ \| & & \| \\ \mathrm{X{\cdot}C{\cdot}H} & & \mathrm{Br{\cdot}C{\cdot}X} \end{array}$$

*trans-trans*
m. p. 89°
(II.)



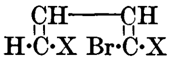
$$\begin{array}{cc} \mathrm{CH} & \!\!\text{——}\!\! & \mathrm{CH} \\ \| & & \| \\ \mathrm{H{\cdot}C{\cdot}X} & & \mathrm{X{\cdot}C{\cdot}Br} \end{array}$$

*cis-cis*
m. p. 68°
(III.)



$$\begin{array}{cc} \mathrm{CH} & \!\!\text{——}\!\! & \mathrm{CH} \\ \| & & \| \\ \mathrm{X{\cdot}C{\cdot}H} & & \mathrm{X{\cdot}C{\cdot}Br} \end{array}$$

*cis-trans*
m. p. 55°
(IV.)



$$\begin{array}{cc} \mathrm{CH} & \!\!\text{——}\!\! & \mathrm{CH} \\ \| & & \| \\ \mathrm{H{\cdot}C{\cdot}X} & & \mathrm{Br{\cdot}C{\cdot}X} \end{array}$$

*cis-trans*
(V.)

$X = CO_2Me$

Towards reducing agents, the three isomerides behave very differently. The *trans-trans*-form is reduced, on heating for a few minutes with zinc and alcohol, to *trans-trans*-methyl muconate and with zinc and acetic acid to methyl $\Delta^{\beta}$-dihydromuconate. The *cis-cis*-form remains unreduced after prolonged treatment with these reagents, whilst the *cis-trans*-form readily gives an almost quantitative yield of methyl $\Delta^{\beta}$-dihydromuconate after short heating with zinc and acetic acid, although it is not reduced by zinc and alcohol.

If it be taken that the oxygen of the carboxyl group plays an important part in the reduction of such unsaturated compounds, the experimental results are such as might have been expected to arise from the purely steric effect of the geometrical configuration : indeed it would seem that reduction is governed by the accessibility of the carboxyl group. It would appear probable, therefore, that the *cis-trans*-form (IV) was the one actually obtained and investigated and that the alternative form (V), if obtained, would be reducible to methyl muconate by zinc and alcohol.

## II. *Dihalogenated Muconic Esters.*

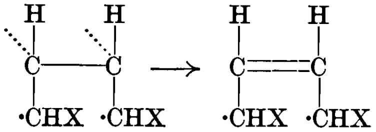
In this series, the three geometrical forms of ethyl αα′-dibromomuconate (*loc. cit.*) have been submitted to reduction. Each of the isomerides was reduced by zinc and acetic acid with such vigour and completeness that discrimination between the isomerides as to reducibility was impossible; the product in each case was ethyl dihydromuconate. A similar result was obtained with the two known forms of ethyl αα′-dichloromuconate (*loc. cit.*, p. 2544). There was the interesting result, however, that none of the three dibromo-esters was readily reduced (bromine replaced by hydrogen) with zinc and alcohol. Such a variation from the mode of reactivity of the monobromo-esters probably reflects the difference between a balanced and an unbalanced molecule.

## III. *Muconic Esters.*

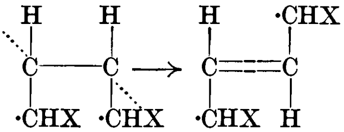
Reduction of *trans-trans*- and *cis-cis*-methyl muconate proceeds so slowly with reagents such as zinc and acetic acid that discrimination between their reducibility is impossible. With palladium and hydrogen, both forms are reduced to methyl adipate.

In all the preceding reductions the dihydrogenated product has been of one form (presumably *trans*-) entirely. Thus, almost quantitative yields of ethyl dihydromuconate (m. p. 2°) and methyl dihydromuconate (m. p. 16°) have been obtained repeatedly; no trace of a second form has been recognisable on any occasion. Since numerous attempts to isolate a second geometrical form, including the removal of bromine from the stereoisomeric methyl and ethyl ββ′-dibromoadipates, have been unsuccessful, it appears certain that such a form can only have a very low degree of stability or is incapable of existence.

There appears no very obvious relationship between the geometrical form of the system $\mathrm{C{:}C{\cdot}C{:}C}$ and that of its reduction product $\mathrm{CH{\cdot}C{:}C{\cdot}CH}$; this is the case whether the process be represented on the Thiele, the Lowry, or the electronic plan. If represented in the van 't Hoff manner, reduction could yield *cis*- and *trans*-isomerides only by variation in the linking of the free valencies. Thus the two ways (A) and (B) are possible. Where *cis*- and *trans*-forms are of comparable stability, both isomerides might be expected to arise in the reduction of any one of the isomeric muconic forms.



(A.)



(B.)

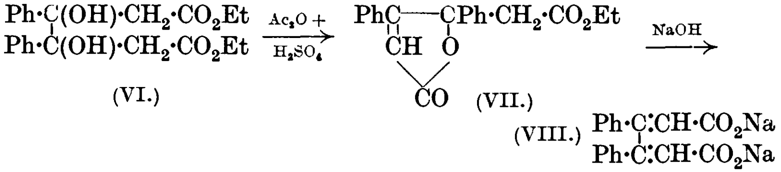
Departure from this equal favouring of *cis*- and *trans*-dispositions (subject to subsequent inversion processes due to experimental conditions) might arise (*a*) by the steric effects of the terminal groups tending towards *trans*-forms, and (*b*) by a tendency towards symmetrical disposition of free valencies as in (B) above, also tending to the production of *trans*-forms. If the effect of terminal addition is gained merely by the occurrence of a secondary effect, a process of molecular rearrangement, then the tendency (probably largely steric) towards stability might be expected to result in the appearance of *trans*-forms. The persistent occurrence of a single form of dihydromuconic ester in the foregoing reductions would seem to be the logical result, were it not for the failure of methods other than reduction to yield the geometrical isomeride. In extending observations to other muconic systems, an instance was discovered in which the form of the reduction product was dependent on that of the parent compound.

### IV. ββ′-*Diphenylmuconic Esters.*

From ethyl *meso*-ββ′-diphenyl-ββ′-dihydroxyadipate Beschke (*Annalen*, 1912, **384**, 143) obtained two diphenyldihydromuconic acids related either as *cis*- and *trans*- or as $\Delta^{\alpha}$- and $\Delta^{\beta}$-isomerides. On re-examination, Beschke's acids proved to be *cis*- and *trans*-forms of the $\Delta^{\beta}$-acid; both yielded benzoylacetic acid as the sole isolable oxidation product when treated with ozone in alkaline solution :

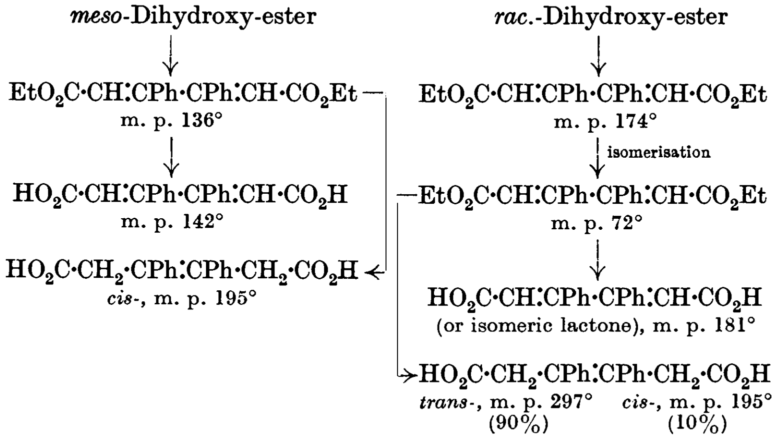
$$HO_2C{\cdot}CH_2{\cdot}CPh{:}CPh{\cdot}CH_2{\cdot}CO_2H \xrightarrow{O_3} 2COPh{\cdot}CH_2{\cdot}CO_2H.$$

The higher-melting acid has the *trans*-configuration, since Beschke showed that this form only could be converted into dihydroxychrysene. In Beschke's synthesis a sodium diphenylmuconate (VIII) was obtained from the dehydration product (VII) of the *meso*-dihydroxy-ester (VI).



(VI.) (VII.) (VIII.)

This substance reverted to the lactone on acidification, but yielded through the silver salt an ethyl diphenylmuconate, m. p. 72°; reduction with sodium-amalgam gave a mixture of the two dihydro-acids (90% *trans*, 10% *cis*). The genesis of these acids became clearer when both dihydroxy-esters were submitted to dehydration under mild conditions. The two stereoisomerides then yielded different forms of ethyl diphenylmuconate, of which that derived from the *racemic* ester passed spontaneously, on short standing, into a third isomeride which proved to be identical with Beschke's ester. The production of the last from a *meso*-compound must have involved stereoisomeric inversion, due to the somewhat drastic conditions employed. Each of the stable esters yielded a corresponding acid on hydrolysis with sulphuric acid; each gave a characteristic product on reduction with sodium amalgam. Isomeric change of the unstable form was too rapid to allow of its reduction product being differentiated from those of its isomerides. It is impossible from the evidence obtained to assign formulæ to the three ethyl diphenylmuconates produced. All attempts to discover their individual configurations by oxidative processes (compare Behrend and Heyer, *Annalen*, 1919, **418**, 294) were unsuccessful owing to their great resistance to oxidation. It is quite clear, however, that the form of the reduction product has a definite relation to that of the parent butadiene compound; whether this is a necessary and fundamental result of the mechanism of reduction or merely a peculiarity arising from the nature of the substituent groups in these substances can only be determined by an examination of other examples. A pronounced steric effect capable of deciding the configuration of the reduction product might be expected to lead to the formation of the same stable reduced form from all the isomeric butadiene esters, not to different forms of comparable stability. On the other hand, it is probable that the spontaneous isomerisation noted above is a volume effect of the kind



$$\begin{matrix}\mathrm{Ph{\cdot}C}{-} \\ \| \\ \mathrm{EtO_2C{\cdot}C{\cdot}H}\end{matrix} \longrightarrow \begin{matrix}\mathrm{Ph{\cdot}C}{-} \\ \| \\ \mathrm{H{\cdot}C{\cdot}CO_2Et}\end{matrix}$$

rather than the reverse.

## EXPERIMENTAL.

*Methyl Muconate Dibromide.*—The gradual addition of bromine (1 mol.) to *trans-trans*-methyl muconate in chloroform solution in direct sunlight gave a product, isolated by evaporation of the solvent in a vacuum, consisting of two isomeric *dibromides* in the approximate proportion 12 : 1, which were separated by fractional crystallisation from ethyl alcohol or petroleum (b. p. 60—80°). The less soluble, more abundant form crystallised in stout, colourless prisms, m. p. 104—105° (Found: Br, 48·35. $C_8H_{10}O_4Br_2$ requires Br, 48·4%), the more soluble form as a coarse powder, m. p. 50° (Found: Br, 48·4%).

*Isomeric Methyl α-Bromomuconates.*—Dry ethereal solutions of the isomeric dibromides were treated in turn with ethereal diethylamine in slight excess. Diethylamine hydrobromide separated rapidly and quantitatively in each case. The ethereal solutions, freed from base by washing with dilute acid, yielded, on evaporation, colourless oils which solidified completely. The product from the more fusible dibromide was homogeneous; it crystallised from ethyl alcohol or petroleum in long, stout needles, m. p. 89° (Found : Br, 31·95. $C_8H_9O_4Br$ requires Br, 32·1%).

The less fusible dibromide yielded a mixture of isomeric monobromo-esters. These were separated completely only by a prolonged and laborious process of fractional crystallisation, using ethyl alcohol and petroleum (b. p. 60—80°) alternately. The less soluble of these isomerides crystallised from alcohol or petroleum in stout prisms, m. p. 68° (Found : Br, 32·1%); the more soluble crystallised from alcohol in small, compact prisms, m. p. 55° (Found : Br, 31·9%). It is a remarkable fact that, although these isomerides were stable when pure, mixtures of the two lower-melting forms invariably changed in a few days to a viscous, pale yellow oil, no longer crystallisable. Removal of hydrogen bromide from the two methyl muconate dibromides could also be accomplished by the use of excess of hot pyridine or the calculated quantity of cold alcoholic sodium methoxide.

*Formation of Amides from Isomeric Methyl α-Bromomuconates.*—Equal quantities of the three isomerides were treated with excess of concentrated aqueous ammonia at room temperature. The esters gradually dissolved, with the separation of crystalline amides. The approximate times of conversion are shown in the table below :

| Bromo-ester. M. p. | Suggested form. | Comparative solubility in organic solvents. | Time of conversion into amide. | Amide. M. p. |
|---|---|---|---|---|
| 89° | *trans-trans* | Most insoluble | 4 hours (no decomp.) | 235° |
| 68 | *cis-cis* | | 9 hours (gross decomp.) | 197 |
| 55 | *cis-trans* | Most soluble | 2½ hours (no decomp.) | 156 |

The *trans-trans*-amide (m. p. 235°) crystallised from water as a colourless powder (Found : Br, 36·5. $C_6H_7O_2N_2Br$ requires Br, 36·5%); the *cis-cis* (m. p. 197°) in stout prisms (Found : Br, 36·4%); the *cis-trans* in long needles (Found : Br, 36·6%).

*Reduction of Methyl α-Bromomuconates.*—(a) *With zinc and acetic acid.* To the ester, dissolved in glacial acetic acid, excess of zinc dust was added in small quantities. The mixture was heated on a steam-bath for 20 minutes, cooled, poured into water, and filtered. The ethereal extract of the filtrate was freed from acetic acid and dried, and the solvent evaporated.

The *trans-trans*-ester was readily reduced: the product, which solidified on cooling, crystallised from light petroleum in well-formed, colourless prisms, m. p. 16°, which obviously represented only one of the two possible geometrical forms of *methyl* $\Delta^{\beta}$*-dihydromuconate* (Found: C, 55·7; H, 7·0. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%). Only the slightest trace of non-crystallisable ester remained in the solvent. Bromination of this ester in chloroform solution gave an almost quantitative yield of the methyl ββ′-dibromoadipate, m. p. 93° (*loc. cit.*, p. 2541). Hydrolysis with dilute sulphuric acid yielded pure $\Delta^{\beta}$-dihydromuconic acid.

The reduction of the *cis-cis*-ester was attempted in a similar fashion. The product after 20 minutes' heating was an oil which did not solidify. On distillation, it was obtained as a colourless oil of boiling point and composition differing little from those of the original compound. Further treatment with zinc and acetic acid for 1 hour yielded a similar oil with a large bromine content. Inability to crystallise these products probably arose from admixture of slight quantities of reduction products; it was frequently found that mixtures of the isomeric bromo-esters with small amounts of impurities could be solidified only with the utmost difficulty.

Reduction of the *cis-trans*-ester to methyl $\Delta^{\beta}$-dihydromuconate, m. p. 16°, proceeded exactly as with the *trans-trans*-form. In this case also, only one geometrical form of the reduced product could be isolated.

(b) *Zinc and alcohol* (*or acetone*). The *trans-trans*-monobromo-ester was refluxed with acetone and excess of zinc dust. Crystals of *trans-trans*-methyl muconate soon separated from the boiling solution. After ½ hour the suspended methyl muconate was redissolved by addition of more acetone, and the resulting solution filtered. The filtrate gave, on evaporation, an almost quantitative yield of methyl muconate, which crystallised from methyl alcohol in the characteristic, long needles, m. p. 156°.

The *cis-cis*-ester was treated similarly, but was recovered unchanged. The bulk of the *cis-trans*-ester was recovered in pure condition after treatment in this way: if any reduction occurred, it was insignificant in extent.

*Reduction of Isomeric Ethyl* αα′*-Dibromomuconates.*—These substances were prepared as described in Part II of this series (*loc. cit.*). Each of the three isomerides passed almost quantitatively into ethyl dihydromuconate on treatment with zinc and acetic acid as above. A careful examination of the reduction product was made in each case. Hydrolysis with dilute sulphuric acid yielded only $\Delta^{\beta}$-dihydromuconic acid, m. p. 197°, and recrystallisation from light petroleum yielded pure *ethyl* $\Delta^{\beta}$*-dihydromuconate* (presumably *trans*-) in colourless prisms, m. p. 2° (approx.). From the mother-liquor, only a very small quantity of non-crystallisable ester was obtained. This, on hydrolysis, also yielded dihydromuconic acid, m. p. 197°.

With zinc dust and alcohol (or acetone), no appreciable reduction was effected in ½ hour. Each of the three isomerides was recovered practically quantitatively.

*Reduction of Isomeric Ethyl* $\alpha\alpha'$*-Dichloromuconates.*—The two known isomerides (*loc. cit.*, p. 2540) were similarly treated with zinc dust and acetic acid. Rapid and complete reduction to ethyl $\Delta^{\beta}$-dihydromuconate was effected. Again, only one form (m. p. 2° approx.) of this substance could be isolated.

*Reduction of Isomeric Methyl Muconates.*—(a) *With zinc and acetic acid.* Reduction of the two known isomerides (*loc. cit.*, p. 2546) proceeded so slowly with zinc and acetic acid that isomerisation of the lower-melting form probably preceded reduction. The product in each case was methyl $\Delta^{\beta}$-dihydromuconate, m. p. 16°, or the corresponding acid.

(b) *With sodium amalgam.* The reduction of the *trans-trans*-acid (corresponding to the methyl ester, m. p. 156°) has previously been described. The product is entirely $\Delta^{\beta}$-dihydromuconic acid, m. p. 197°. Methyl muconate, m. p. 75°, was hydrolysed with alkali to a mixture of the corresponding acid and lactone (*loc. cit.*, p. 2548), which was reduced in the usual way with sodium amalgam in a current of carbon dioxide. The product yielded $\beta\beta'$-dihydromuconic acid, m. p. 197°, only.

(c) *With palladium and hydrogen.* The two isomerides yielded methyl adipate when reduced at atmospheric pressure by the method of Skita. Reduction to the dihydro-stage could not be secured by restricting the hydrogen supplied: in this case a portion of the ester remained unreduced.

*Action of Zinc on Isomeric Methyl* $\alpha\alpha'$*-Dibromoadipates.*—The two dibromo-esters (*loc. cit.*, p. 2541) were each dissolved in acetone and carefully treated with excess of zinc dust. Reaction, which took place rapidly, was completed by heating for a short time on a steam-bath. The product, isolated in the usual way, was in each case methyl $\Delta^{\beta}$-dihydromuconate, m. p. 16°.

*Ethyl* $\beta\beta'$*-Diphenyl-*$\beta\beta'$*-dihydroxyadipate.*—The *meso*- and *racemic* forms of this ester were obtained in essentially the way described by Beschke (*loc. cit.*); magnesium, however, was employed instead of zinc, the reaction being started by addition of a crystal of iodine.

*Action of Phosphorus Halides on Dihydroxy-esters.*—Both *meso*- and *racemic* forms yielded, when allowed to stand for 24 hours with the calculated amount (2 mols.) of phosphorus tribromide, diphenylmuconic esters. Simple replacement of hydroxyl by bromine could not be effected, the bromine content of the product never rising to 1%. The *meso*-ester (m. p. 168°) yielded invariably and solely an *ethyl* ββ′-*diphenylmuconate* which crystallised from benzene or alcohol in short prisms, m. p. 136° (Found: C, 75·6; H, 6·3. $C_{22}H_{22}O_4$ requires C, 75·5; H, 6·3%). The *racemic* ester (m. p. 137°) similarly yielded a second, more soluble form of the same ester which crystallised from the same solvents in well-defined needles, m. p. 174° (Found: C, 75·6; H, 6·3%).

Treatment of benzene solutions of the hydroxy-esters with phosphorus pentabromide or pentachloride gave similar results. Moderation of the reaction by cooling to 0° did not prevent the removal of hydrogen bromide.

*Isomerisation of Ethyl Diphenylmuconate,* m. p. 174°.—The pure dry ester, when allowed to stand in the air for 15 minutes, became sticky. Recrystallisation at this stage yielded a mixture of ethyl diphenylmuconates, m. p.'s 174° and 72°. When the sticky mass was allowed to stand longer (45 minutes), it set to a glassy solid which crystallised from alcohol in small needles, m. p. 72° (Found: C, 75·55; H, 6·3%). Yield 95%. The rapid isomerisation of the form, m. p. 174°, prevented satisfactory observations of the geometrical form of its reduction product.

*Preparation of Isomeric Ethyl* ββ′-*Diphenylmuconates.*—For the preparation of considerable quantities of these esters the phosphorus halide method was inconvenient. The following methods were therefore employed.

(*a*) The dihydroxy-ester was refluxed with zinc dust (3 parts) and absolute alcohol (8—10 parts) for 6 hours. In the case of the *meso*-ester, crystallisation of ethyl diphenylmuconate (m. p. 136°) from the hot filtered solution commenced at once; with the *racemic* ester, concentration was necessary before the unstable form (m. p. 174°) separated. This process gave excellent results with the pure dihydroxy-esters.

(*b*) The dihydroxy-ester was boiled for 1 hour with acetic anhydride and the product was cooled and extracted with petroleum (b. p. 80—100°) (in which acetic anhydride is not very soluble). Evaporation of the solvent and cooling of the residue to 0° caused crystallisation of the dehydrated ester. This method was usually employed for treating the residual sludge of the "Reformatski" product. This contained a considerable quantity of difficultly recoverable *racemic* ester which yielded directly, on dehydration for 24 hours, a crystalline product purifiable by one recrystallisation.

ββ′-*Diphenylmuconic Acid.*—Hydrolysis of ethyl diphenylmuconate, m. p. 136°, with dilute sulphuric acid yielded the corresponding acid, which separated from alcohol as a white, crystalline powder, m. p. 142° [Found : C, 73·1; H, 4·7; *M* (dibasic), 298. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·7%; *M*, 294]. The isomeric ester, m. p. 72°, yielded, on similar treatment, an acid, m. p. 181°. This also separated from alcohol as a white, crystalline powder (Found : C, 73·6; H, 4·7%; equiv., 221) and was probably identical with Beschke's 2 : 3-diphenylcrotonolactone-3-acetic acid.

*Reduction of Isomeric Ethyl Diphenylmuconates.*—The two stable esters were separately hydrolysed by adding a hot aqueous solution of caustic soda to a boiling alcoholic solution of the ester until permanent alkalinity was secured. After the alcoholic liquor had been boiled for 1 hour, the precipitated sodium salt was filtered off and dissolved in a small quantity of water. Gradual addition of 3% sodium amalgam until effervescence ceased, followed by filtration and acidification, gave an immediate precipitate of the reduced acid. cis-ββ′-*Diphenyl-*$\Delta^{\beta}$*-dihydromuconic acid,* the sole product from ethyl diphenylmuconate (m. p. 136°), crystallised from water in colourless prisms, m. p. 195° (Found : C, 72·9; H, 5·2. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·3%). trans-ββ′-*Diphenyl-*$\Delta^{\beta}$*-dihydromuconic acid,* which was produced together with its isomeride from ethyl diphenylmuconate (m. p. 72°), crystallised from alcohol in colourless prisms, m. p. 297° (Found : C, 72·9; H, 5·3%). The *ethyl* esters of the *cis-* and *trans*-acids, obtained by saturating alcoholic solutions with hydrogen chloride, crystallised from alcohol in colourless prisms, m. p. 56° and 86°, respectively.

*Oxidation of* $\Delta^{\beta}$*-Diphenyldihydromuconic Acids.*—Each of the acids (3 g.) was separately dissolved in a slight excess of dilute sodium carbonate solution and treated with a rapid current of ozonised oxygen for 48 hours. After air had been bubbled through the brown liquids to remove dissolved ozone, the products were acidified and extracted with ether. The ethereal extract contained in each case a mixture of unchanged acid and benzoylacetic acid, which were separated by fractional crystallisation from benzene and petroleum. The benzoylacetic acid derived from each acid, after the final crystallisation from alcohol, melted and decomposed at 103—104° and gave a violet-red coloration with ferric chloride (Found : C, 65·7; H, 4·9. Calc. : C, 65·8; H, 4·9%).

The authors desire to acknowledge grants from the Government Grant Committee of the Royal Society (to E. H. F.) and the Chemical Society (to W. M. D.) towards the expenses of this research.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.
[*Received, December 2nd,* 1926.]