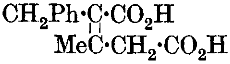
358. *The Structure of the Glutaconic Acids and Esters. Part V. α-Benzyl- and α-Benzyl-β-methyl-glutaconic Acids.*

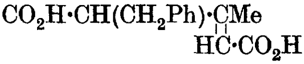
By G. A. R. KON and E. M. WATSON.

THE structures of the two isomeric α-benzyl-β-methylglutaconic acids, the stable forms of which are, respectively, the *cis*-αβ (I) and the *trans*-βγ (II) isomeride, have been established (this vol., p. 1).

(I.)



$$\begin{array}{l} CH_2Ph\cdot C\cdot CO_2H \\ \qquad\;\;\, \| \\ \qquad MeC\cdot CH_2\cdot CO_2H \end{array}$$



$$\begin{array}{r} CO_2H\cdot CH(CH_2Ph)\cdot CMe \\ \| \quad\;\; \\ HC\cdot CO_2H \end{array}$$

(II.)

The object of the present work was to prepare the other two possible isomerides: the interconversion of the two stable forms has also been investigated and their reactions compared with those of the corresponding acids without a β-substituent.

The method of synthesising the two stereoisomeric βγ-esters already indicated (*loc. cit.*) is based on the supposition, since verified by further experiments, that an ester such as ethyl β-methylglutaconate forms a potassio-derivative without change of configuration. This follows because the ester is recovered unchanged on acidification and then gives on hydrolysis the pure individual acid from which it was derived. The potassio-derivative can be converted into an alkyl derivative which must be the βγ-unsaturated ester: *e.g.*, the *cis*- and the *trans*-form of ethyl α-benzyl-β-methylglutaconate should be formed from the two isomeric β-methylglutaconic esters.

Benzylation is slow unless heat is applied, and this leads to considerable isomerisation. The operation, however, can be conducted at room temperature and completed by addition of a more active alkylating agent such as methyl iodide; the product is a readily separable mixture of α-methyl and α-benzyl esters.

Ethyl *trans*-β-methylglutaconate has thus been benzylated, giving an ester identical with that obtained by esterification of the acid (II). Similar treatment of ethyl *cis*-β-methylglutaconate leads to an ester of appreciably different physical properties (notably a lower refractive index). Oxidation with ozone shows that both esters are pure βγ-unsaturated esters, but whereas the *trans*-ester is hydrolysed by dilute hydrochloric acid to the pure *trans*-acid (II) the *cis*-ester on similar treatment is converted into the *cis*-αβ-acid and not into the still unknown *cis*-βγ-acid. This change provides a striking example of a change of structure without change of configuration.

The opposite type of transformation, from the *cis*-αβ-acid to a new isomeride, the trans-αβ-*acid*, has been achieved by ultra-violet irradiation, the change of configuration being analogous to the changes of the stable cinnamic acid derivatives into their *allo*-modifications (compare Stoermer, Grimm, and Laage, *Ber.*, 1917, **50**, 966). The new acid melts without decomposition 10° higher than its isomeride and is characterised by a soluble barium salt; it is comparatively unstable, being quickly converted by acids into the *cis*-form. It has, however, been converted into the ester, which has a higher density than any of its isomerides and on ozonisation gives the products to be expected from a pure αβ-ester.

All the four possible α-benzyl-β-methylglutaconic esters have thus been prepared, and three out of the four possible acids. All attempts to convert the *trans*-βγ-acid into a *cis*-form by irradiation have been unsuccessful.

The two stable acids in this series are readily interconvertible and this conversion has been studied in some detail. The two acids can be quantitatively separated by means of their barium salts. Acids convert the *trans*-βγ-acid into the *cis*-αβ, and alkalis have the reverse effect, the change being apparently complete in each case.

Such a result is interesting and unexpected, for in many tautomeric substances examined in these laboratories the position of equilibrum is independent of the equilibrating agent used. The nature of this equilibrium must, in the present instance, depend on a combination of several factors which are variously affected by the nature of the catalyst. Concentrated hydrochloric acid, which is frequently employed to convert *cis*- into *trans*-isomerides, actually converts the *trans*-acid into the *cis*-form. Dilute hydrochloric acid has, apparently, no effect on the *trans*-acid and can be used to hydrolyse its ester. On the other hand, even very weak (2·5%) alkali causes isomerisation of the *cis*-acid: experiments conducted under Linstead's standard conditions (J., 1927, 2579) indicate that the mobility of this acid is approximately 15.

It was suggested in our previous paper (*loc. cit.*) that the potassio-derivative obtained from either the *cis*-αβ- or the *trans*-βγ-ester is probably a derivative of the αβ-ester and that the small amount of benzylidene ester formed is produced from it at the moment of acidification by the further migration of the proton. The methylation of the potassio-derivative has now been examined; and the new ester gives, on ozonisation, ethyl methylacetoacetate and ethyl pyruvate, without any trace of benzaldehyde. It can therefore be concluded that the potassio-derivative has, as originally anticipated, the structure (III) and the methylated ester must be (IV),

(III.) $CO_2Et{\cdot}C(CH_2Ph){:}CMe{\cdot}CHK{\cdot}CO_2Et$
(IV.) $CO_2Et{\cdot}C(CH_2Ph){:}CMe{\cdot}CHMe{\cdot}CO_2Et$

and that the formation of the benzylidene ester must be regarded as taking place as suggested above. The methylation is not complete and the pure acids corresponding to the ester (IV) have not yet been obtained. The benzyldimethyl ester has also been prepared by the benzylation of αβ-dimethylglutaconic ester. This should give rise to the isomeric βγ-ester, $CO_2Et{\cdot}CH(CH_2Ph){\cdot}CMe{:}CMe{\cdot}CO_2Et$; the product isolated does consist very largely of this ester, but also contains a certain amount of the ester (IV).

We have also extended the investigation to the α-benzylglutaconic acids. Two isomeric acids are known, the *trans*-acid, m. p. 154°, and the "labile" acid, m. p. 139°, prepared by Thole and Thorpe (J., 1911, **99**, 2208); there is no record in the literature of any attempt to establish the structure of these compounds.

The higher-melting acid has now been oxidised with permanganate, giving oxalic acid and benzaldehyde. The latter is evidently formed by the oxidation of the phenylated acid (probably benzylmalonic) originally formed, a change frequently observed in similar cases (compare Michael and Garner, *Amer. Chem. J.*, 1906, **35**, 265), and the acid therefore has the βγ-structure (V). Similarly, the ester obtained from it is practically the pure βγ-compound, giving ethyl glyoxylate (and oxalic acid) and ethyl formylbenzylacetate as the chief products of ozonisation.

The isomeric *cis*-acid melts at 149—150° when pure, but mere crystallisation from water is sufficient to cause partial isomerisation to a eutectic mixture, m. p. 139°, evidently identical with Thole and Thorpe's "labile" acid. The pure *cis*-acid gives no trace of oxalic acid on oxidation with permanganate and, if suitable precautions are taken, the formation of phenylpyruvic acid can be clearly demonstrated. The *cis*-acid, therefore, has the αβ-structure (VI) and it is safe to infer that the hydroxy-anhydride has the double bond in the same position.

$CO_2H{\cdot}CH(CH_2Ph){\cdot}CH{:}CH{\cdot}CO_2H$ (V.)

$CO_2H{\cdot}C(CH_2Ph){:}CH{\cdot}CH_2{\cdot}CO_2H$ (VI.)

This conclusion had already been reached by Thole and Thorpe (*loc. cit.*), who isolated oxalic acid on oxidation with permanganate. This, together with benzaldehyde, has also been obtained in the present work. Neither product, however, definitely establishes the structure of the hydroxy-anhydride, because the oxidation is carried out in alkaline solution in which both products could be obtained from either form.'

The mobility of this acid is so high that it is impossible to esterify it without isomerisation; the ester obtained consists mainly of the βγ-ester, but contains some αβ and a certain amount of α-benzylideneglutaric ester, $CO_2Et{\cdot}C({:}CHPh){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$, evidently produced from the αβ-ester. A similar mixture of esters is obtained when the βγ-ester is converted into its potassio-derivative and this is treated with benzoic acid or a mineral acid; the presence of the benzylidene ester is recognised by the formation of benzaldehyde on oxidation with ozone and the corresponding acid is isolated in small amount on hydrolysis of the ester. In these esters we therefore have an approach to the state of affairs anticipated by Feist (*Annalen*, 1922, **428**, 25), who suggested that the esters of the glutaconic acids are desmotropic mixtures although the acids are pure individuals.

The *trans*-βγ-acid is stable to both acid and alkali: the *cis*-αβ-acid can properly be described as the labile isomeride. The equilibrium in the esters is similarly on the side of the βγ-form. The metallic derivatives, such as the potassio-ester, are, however, derived from the αβ-ester, just as they are in the α-benzyl-β-methylglutaconic esters; these give rise to a γ-methyl derivative (VII).

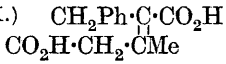
$$CO_2Et\cdot C(CH_2Ph){:}CH\cdot CHMe\cdot CO_2Et \quad \text{(VII.)}$$

$$CO_2Et\cdot CH(CH_2Ph)\cdot CH{:}CMe\cdot CO_2Et \quad \text{(VIII.)}$$

The new ester is actually a mixture of the αβ- and the βγ-isomeride, the latter (VIII) predominating; on hydrolysis with either alkaline or acid reagents the same pure acid, m. p. 185°, is obtained. This is undoubtedly a *trans*-form and oxidation of the ester prepared from it shows that it is the pure βγ-compound (VIII); we have so far failed to prepare its αβ-isomeride, because all efforts to obtain the corresponding anhydride were unsuccessful and the *trans*-acid itself is stable to both alkalis and acids, like its lower homologue.

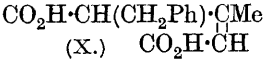
A comparison of the stable isomerides of the different α-benzyl-substituted acids suggests that one, at any rate, of the factors which influence stability is the symmetry of the molecule. Thus, in the α-benzyl-β-methyl acids, the most evenly balanced systems are clearly the *cis*-form of the αβ-acid (I) and the *trans*-form of the βγ-acid (II), whilst their stereoisomerides have the two heavy substituents on the same sides of the doubly-bound carbons; this arrangement should be particularly unstable in the *cis*-form (X), as is actually the case.

(IX.)



$$\begin{array}{r} CH_2Ph\cdot C\cdot CO_2H \\ \| \quad\;\; \\ CO_2H\cdot CH_2\cdot CMe \quad\;\; \end{array}$$

(X.)



$$\begin{array}{r} CO_2H\cdot CH(CH_2Ph)\cdot CMe \\ \| \quad\;\; \\ CO_2H\cdot CH \end{array}$$

The same considerations apply to the α-benzyl- and the α-benzyl-γ-methylglutaconic acids; the absence of the stabilising influence of a β-substituent is clearly seen in the comparative instability of the *cis*-αβ-acid. The αβ-forms are in any case the less favoured, a conclusion contrary to Thole and Thorpe's statement (*loc. cit.*) that the βγ-forms are unstable.

EXPERIMENTAL.

Benzylation of Ethyl β-Methylglutaconate.—The two stereoisomeric forms of ethyl β-methylglutaconate were prepared and converted into their potassio-derivatives as described in our previous paper (*loc. cit.*).*

Each potassio-compound was suspended in dry C_6H_6 and left with an excess of CH_2PhCl at room temp. for a month, with occasional shaking: an excess of MeI was then added. A fortnight later, the reaction appeared to be complete, a test portion added to H_2O giving a neutral reaction. The C_6H_6 solution was mixed with Et_2O, washed with H_2O, dried, and evaporated, and the residue fractionated under reduced pressure. The ester obtained from the *trans*-form had b. p. 191°/11 mm., $d_{4°}^{18\cdot6°}$ 1·0664, $n_D^{18\cdot6°}$ 1·5089, whence $[R_L]_D$ 81·25; that from the *cis*-form had b. p. 192°/11 mm., $d_{4°}^{19\cdot9°}$ 1·0644, $n_D^{19\cdot9°}$ 1·5054, whence $[R_L]_D$ 80·92.

Ozonisation. 8 G. of each of the above esters were treated with O_3, and the products isolated as described in Part II (*loc. cit.*). Both esters gave identical results. The aq. and alkaline washings contained much $H_2C_2O_4$. The neutral portions gave the following fractions at 13 mm.: (1) below 120°, less than 0·1 g., giving a purplish-red colour with $FeCl_3$; (2) above 120°. This constituted the whole of the distillate which boiled mainly between 140° and 160°; it gave a clear purple colour with $FeCl_3$ (the neutral oil before distillation gave a colour faintly tinged with green due to traces of ethyl phenylpyruvate) and consisted of ethyl benzylacetoacetate, which was identified by its semicarbazone and the formation of phenylbenzylmethylpyrazolone.

The esters were thus pure βγ-forms, although the presence of the αβ-form in traces is not excluded.

Hydrolysis. When hydrolysed by 10% HCl, the *trans*-βγ-ester gave the pure *trans*-βγ-acid; no trace of insol. Ba salt was obtained by dissolving it in NH_3 aq. and boiling the solution with $BaCl_2$. Under identical conditions, the *cis*-βγ-ester gave the *cis*-αβ-acid, m. p. 148°, the *cis*-βγ-acid being evidently unstable and completely isomerised.

Ultra-violet Irradiation.—A solution of the *trans*-βγ-acid, m. p. 134°, in dry C_6H_6 was continuously irradiated in a flattened quartz flask by means of a Hg vapour lamp for 10 days. Some charring occurred, but only unchanged *trans*-βγ-acid was recovered. The *cis*-αβ-acid was similarly treated in hot H_2O (it was too sparingly sol. in C_6H_6). The product was concentrated under reduced press.; the first crop of crystals consisted of unchanged *cis*-αβ-acid, but on further concn. a new acid was obtained as an oil which gradually solidified and could be purified by recrystn. from H_2O. In subsequent preps., the *cis*-acid was irradiated for 21 days; the change was then complete, although there was appreciable decomp.

The new acid, trans-*α-benzyl-β-methyl-*Δ^{α}*-propene-αγ-dicarboxylic acid*, crystallised from H_2O in fine needles, m. p. 157—158°; its Ba salt is sol. in H_2O. It is very sensitive to mineral acids and cannot be liberated from its salts without undergoing change; a few mins.' boiling with 10% HCl converts

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* The original esters could be regenerated unchanged from the potassio-derivatives by means of $Ph\cdot CO_2H$ in a neutral solvent and we have confirmed their structure by hydrolysis to the pure acids by means of very dil. alkali in the cold.

it completely into the *cis*-$\alpha\beta$-acid (Found : C, 66·5 ; H, 5·9 ; *M*, dibasic, 235·2. $C_{13}H_{14}O_4$ requires C, 66·6 ; H, 6·0% ; *M*, 234·1).

The ethyl ester was prepared through the Ag salt by the method described in Part II. Its properties, together with those of its three isomerides, are given in the accompanying table :

Ester.	B. p.	*t*.	$d_4^{t°}$.	n_D.	$[R_L]_D$.
cis-$\alpha\beta$	191°/10 mm.	20·0°	1·0702	1·5089	80·95
trans-$\alpha\beta$	195—196/14 mm.	17·8	1·0723	1·5087	80·76
cis-$\beta\gamma$	192/11 mm.	19·9	1·0644	1·5054	80·92
trans-$\beta\gamma$	195/13 mm.	20·0	1·0643	1·5085	81·34

Ozonisation. The *trans*-$\alpha\beta$-ester was ozonised as described in Part II and gave the same products as the *cis*-$\alpha\beta$-ester ; no trace of $H_2C_2O_4$, ethyl glyoxylate, or ethyl benzylacetoacetate could be detected amongst them and it must be concluded that the ester of the acid, m. p. 157—158°, was the pure $\alpha\beta$-ester.

Interconversion of the cis-$\alpha\beta$- *and* trans-$\beta\gamma$-*Benzylmethylglutaconic Acids.*—Iodo- and bromo-metric methods of analysis showed that the $\beta\gamma$-acid was the more reactive, but the difference was not sufficiently great to serve as the basis of a method for the analysis of mixtures. Both acids reacted at once with Br in KBr aq. (Linstead and Mann, J., 1931, 723) and with Br water; they added 85% of the theo. amount of Br in 75% AcOH solution in 5 mins.

Oxidation in $MgSO_4$ and $NaHCO_3$ aq. by $N/100$-$KMnO_4$ and titration of the I subsequently liberated from acidified KI aq. gave erratic results.

The method finally adopted consisted in the pptn. of the *cis*-$\alpha\beta$-acid in the form of its Ba salt. The solubility of this salt in H_2O was roughly determined by boiling a known wt. under the same conditions as those of the estimations and weighing the residue.

The estimations were carried out as follows. About 0·5 g. of the pure *cis*-acid was dissolved in the theo. amount (+ 1 c.c. excess) of about $2N$-NH_3, diluted to 100 c.c., and 5 g. of $BaCl_2$ added. The whole was boiled for 15 mins., the Ba salt separating in a coarsely cryst. condition. Any loss of H_2O by evaporation was made good and, when cool, the Ba salt was collected, washed with H_2O, EtOH, and Et_2O, dried in a steam-oven for 1 hr. and then in vac., and weighed after standing for 15 mins. in the balance case. Under these conditions, the pure acid gave a recovery, after allowance for the solubility of the salt, of 98·5—99%, whilst a typical mixture of the *cis*- and the *trans*-acid containing 54·75% of the former gave a value of 54·2% for the *cis*-acid content.

Equilibrations.—About 1 g. of the *cis*-acid was dissolved in the required amount (11 equivs. of a 25% solution by wt.) of KOH and heated for the required time in a closed tube in boiling H_2O. The reaction was stopped by pouring the whole, with vigorous stirring, into the theo. amount required for exact neutralisation of 10% HCl diluted to 150 c.c. The solution was then made alkaline with 3 c.c. of $2N$-NH_3, 5 g. of $BaCl_2$ were added, the whole was made up to 225 c.c., and the Ba salt of the *cis*-acid was pptd. by 15 mins.' boiling. Any loss of H_2O was then made good and the Ba salt was separated and estimated as above. An approx. determination of the solubility of the Ba salt under these conditions was again made and allowed for in calculating the results.

Solubility of the Ba salt = 0·094 g.

Time (hr.).	Wt. of acid used (g.).	Wt. of Ba salt + 0·094 g.	Wt. of acid equiv.	$k_1 + k_2$.
0·5	1·0867	0·7025	0·4457	1·781
1·0	0·9590	0·3480	0·2208	1·467
1·5	0·9954	0·2040	0·1294	1·360
2·0	1·0534	0·1060	0·0672	1·375
2·5	0·9842	<0·094	<0·0596	—

Mean value for $(k_1 + k_2) = 1·495$
Mobility $= (k_1 + k_2) \times 10 = 15$

Action of Hydrochloric Acid on the trans-*βγ-Acid.*—The acid (3 g.) was boiled under reflux with 100 c.c. of conc. HCl for 44 hrs. The cooled liquid was neutralised with NH_3, extracted with Et_2O to remove the hydrocarbon formed by decarboxylation of the acid, and treated with $BaCl_2$. When the solution was heated, the cryst. salt of the *cis-αβ*-acid was formed; it was collected, boiled with H_2O, and acidified with HCl aq.; the *cis-αβ*-acid crystallised from the filtered solution on cooling, the amount recovered being 80—85% of the *trans-βγ*-acid taken.

Methylation of α-Benzyl-β-methylglutaconic Ester.—The ester was treated with the theo. amount of dry EtOH-free KOEt and excess of MeI in dry Et_2O. The *product*, isolated in the usual way, distilled at 195—198°/12 mm. and had $d_{4°}^{18·4°}$ 1·0603, $n_D^{18·4°}$ 1·5081 (Found : C, 70·6; H, 7·7. $C_{17}H_{22}O_4$ requires C, 70·3; H, 7·6. $C_{18}H_{24}O_4$ requires C, 71·1; H, 7·9%).

Ozonisation. 8 G. of the ester were ozonised, and the products isolated, as previously described. The aq. and the alkaline washings contained no trace of $H_2C_2O_4$. The neutral portion gave the following fractions at 15 mm. : (1) below 65°; this was small, gave a purplish-red colour with $FeCl_3$, and contained no Ph·CHO. (2) 65—80°; about 1 g., consisting of ethyl acetoacetate and ethyl methylacetoacetate, isolated as phenylmethylpyrazolone and phenylhydrazone respectively. (3) 80—160°, chiefly between 145° and 150°; this made up the rest of the distillate, gave a clear green colour with $FeCl_3$, and consisted of ethyl phenylpyruvate, identified as its semicarbazone. The ester was thus a mixture of the pure *αβ*-forms of α-benzyl-β-methyl- and α-benzyl-βγ-dimethyl-glutaconic esters.

Benzylation of αβ-Dimethylglutaconic Ester.—The ester was refluxed with the theo. amount of EtOH-free KOEt and excess of CH_2PhCl in both dry Et_2O and dry C_6H_6 until neutral; the products were isolated in the usual way. In neither case was benzylation complete, but the benzylated ester was readily separated by fractionation. It had b. p. 190—192°/8 mm., $d_{4°}^{26·8°}$ 1·0548, $n_D^{26·8°}$ 1·5039, whence $[R_L]_D$ 85·38 (Found : C, 70·9; H, 7·7%).

On ozonisation it gave mainly ethyl pyruvate and ethyl benzylacetoacetate, derived from the *βγ*-form of α-benzyl-βγ-dimethylglutaconic ester, but there was also present an appreciable amount of ethyl methylacetoacetate and ethyl phenylpyruvate, derived from the *αβ*-isomeride.

trans-*α-Benzyl-Δ^{β}-propene-αγ-dicarboxylic Acid.*—42 G. of the corresponding tetracarboxylic ester were boiled for 10 hrs. with 126 g. of cryst. $Ba(OH)_2$ and 290 c.c. of H_2O. The mixture was then acidified with HCl aq. and extracted with Et_2O, and the extract washed once with H_2O, dried, and evaporated (compare Guthzeit and Bolam, *J. pr. Chem.*, 1896, **54**, 259). The residue gave pure benzylglutaconic acid, m. p. 154°, after two crystallisations from H_2O.

Oxidation. The acid (about 1 g.), dissolved in Na_2CO_3 aq., was diluted to

300 c.c. and treated at 0° with cold $KMnO_4$ aq. The excess of this was destroyed with H_2O_2, and from the filtered liquid Et_2O extracted Ph·CHO (semicarbazone, m. p. and mixed m. p. 220°, decomp.). The aq. solution was evaporated to dryness: on acidification, the residue gave an almost theo. yield of $H_2C_2O_4$ (titration of Ca salt).

Ethyl trans-*α-Benzyl-Δ^{β}-propene-αγ-dicarboxylate.*—The *trans-βγ*-acid was esterified through its Ag salt; the ester had b. p. 190—191°/12 mm., $d_{4°}^{17\cdot0°}$ 1·0810, $n_{D}^{17\cdot0°}$ 1·5089, $[R_L]_D$ 76·27.

Ozonisation. The ester was ozonised in the usual manner. A quantity of $H_2C_2O_4$ was found in the aq. and $NaHCO_3$ washings; the neutral portion boiled between 120° and 150°/13 mm. The first few drops had the pungent smell characteristic of formyl compounds and gave a red colour with $FeCl_3$, suggesting the presence of ethyl formylacetate; no derivative, however, was isolable. The main part of the distillate gave an intense reddish-purple colour with $FeCl_3$ and contained ethyl formylbenzylacetate, identified by its *semicarbazone*, colourless prisms, m. p. 169°, from MeOH (Found: C, 59·5; H, 6·4. $C_{13}H_{17}O_3N_3$ requires C, 59·3; H, 6·5%). The last few drops of the distillate gave a slight green tinge with $FeCl_3$ before the purple colour developed; this was no doubt due to the presence of ethyl phenylpyruvate, although no derivative of the latter could be isolated.

The ester ozonised thus consisted of the βγ-ester, although it probably contained a small amount of the αβ-isomeride.

Action of potassium ethoxide on the ester. The ester, prepared from crude α-benzylglutaconic acid by esterification with EtOH and H_2SO_4, had b. p. 186°/8 mm., $d_{4°}^{20\cdot0°}$ 1·0800, $n_{D}^{20\cdot0°}$ 1·5073. It was treated with EtOH-free KOEt exactly as described in Part II (*loc. cit.*, p. 6); a solid K derivative separated from petroleum solution but not from Et_2O solution. The ester, regenerated by means of $Ph·CO_2H$, had b. p. 186°/8 mm., $d_{4°}^{20\cdot0°}$ 1·0787, $n_{D}^{20\cdot0°}$ 1·5070.

Both the original ester and the regenerated ester were ozonised; the former gave the same result as the ester described above, although there was a very small low fraction (below 70°) with the odour of Ph·CHO; this was not, however, identified with certainty. The regenerated ester gave a distinct low fraction in which Ph·CHO was identified in the form of its semicarbazone; the highest fraction again gave a greenish colour with $FeCl_3$. Both esters therefore consisted mainly of the βγ-form but contained a little of the αβ-isomeride; the regenerated ester also contained an appreciable amount of ethyl α-benzylideneglutarate.

Hydrolysis. The regenerated ester was left with cold aq.-alc. KOH for 2 days, and the acid isolated. It was recrystallised from acetone, C_6H_6–petroleum, and finally H_2O and proved to be the original acid, m. p. and mixed m. p. 154°; a second acid, m. p. 174—175°, probably α-benzylideneglutaric acid (Fittig and Roedel, *Annalen*, 1894, **282**, 336), was isolated in amount insufficient for investigation.

cis-*α-Benzyl-Δ^{α}-propene-αγ-dicarboxylic Acid.*—The *trans*-acid, m. p. 154°, was converted into the anhydride as described by Thole and Thorpe (*loc. cit.*). The ethereal solution of the anhydride was washed with $NaHCO_3$ aq. until the washings were alkaline. The combined washings, which had a deep magenta colour, were acidified and extracted with Et_2O; the extract on evaporation gave clusters of needles of the cis-*acid*, m. p. 149—150° after crystn. from C_6H_6–petroleum (Found: C, 65·6; H, 5·6; *M*, dibasic, 220·0. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%; *M*, 220·1). The new acid cannot be recrystallised from H_2O without extensive isomerisation to the *trans-βγ*-acid: the first crop of crystals is a eutectic mixture, m. p. about 139°, the m. p. of which is *not* depressed by admixture with either of the pure components; it does not appear possible to resolve it into its components by crystn. from org. solvents. The eutectic, m. p. 139°, is evidently identical with Thole and Thorpe's *cis*-acid. Prolonged boiling with H_2O causes complete conversion of the *cis-αβ*-acid into the *trans-βγ*.

Oxidation. This was carried out in exactly the same way as that of the *trans-βγ*-acid. No Ph·CHO was formed. The acid products isolated by means of Et_2O were solid and consisted of a small amount of unoxidised initial material together with phenylpyruvic acid, which was recognised by the green colour it gave with $FeCl_3$. No $CH_2(CO_2H)_2$ was isolated, as this had been completely decomposed to AcOH; no trace of $H_2C_2O_4$ appeared to have been formed, showing that the acid was the pure *αβ*-compound.

Esterification. The *cis-αβ*-acid was converted into its ester as before; this had b. p. 189—190°/13 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0778, $n_D^{20\cdot0^\circ}$ 1·5068, and was evidently a mixture; it gave ozonisation products derived mainly from the *βγ*-ester, although the isolation of Ph·CHO points to the presence of ethyl *α*-benzylideneglutarate. The ester of the *αβ*-acid is evidently unstable and changes into this equilibrium mixture even under very mild conditions.

Eutectic Mixture, m. p. 139°.—This mixture, obtained as described above, crystallised unchanged from C_6H_6 (Found: *M*, dibasic, 220·0). It was oxidised with $KMnO_4$ and gave the same products as the pure *cis-αβ*-acid, but small quantities of Ph·CHO and $H_2C_2O_4$ were also isolated, showing the presence of the *βγ*-acid.

Esterification. The ester obtained from the eutectic mixture through the Ag salt had b.p. 190—191°/12 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0788, $n_D^{20\cdot0^\circ}$ 1·5074, and was thus very similar to the esters already described. It gave the same products on ozonisation, except that rather less Ph·CHO was obtained.

Oxidation of the Hydroxy-anhydride.—1 G., dissolved in 10 c.c. of 10% $NaHCO_3$ aq. and diluted to 200 c.c., was oxidised as previously described. The Et_2O layer gave, on evaporation, a good yield of Ph·CHO (semicarbazone, m. p. and mixed m. p. 220°, decomp.), whilst the aq. layer, after filtration and evaporation, gave a considerable amount of $H_2C_2O_4$ and a small amount of $Ph{\cdot}CO_2H$.

Methylation of Ethyl α-Benzylglutaconate.—The ester, prepared from the *trans-βγ*-acid by means of EtOH and H_2SO_4, was treated as described on p. 2440. The resulting *ethyl α-benzyl-γ-methylglutaconate* had b. p. 192°/10 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0584, $n_D^{20\cdot0^\circ}$ 1·5022, $[R_L]_D$ 80·94 (Found: C, 70·2; H, 7·7. $C_{17}H_{22}O_4$ requires C, 70·3; H, 7·6%).

Ozonisation. The ester (8 g.) was ozonised and the products were isolated in the usual way. The acid portion was very small and was probably $H_2C_2O_4$ formed from a little unmethylated ester. The neutral portion gave the following fractions at 13 mm.: (1) below 70°, 1·0 g., which had a pungent smell and gave a purple colour with $FeCl_3$, indicating ethyl *α*-formylpropionate; with semicarbazide, however, a practically quantitative yield of the semicarbazone of ethyl pyruvate, m. p. 206°, was obtained (Found: C, 41·8; H, 6·4. Calc. for $C_6H_{11}O_3N_3$: C, 41·6; H, 6·4%). (2) 70—130°, 0·5 g., which consisted of ethyl pyruvate. (3) 130—160°, 3·7 g., consisting of ethyl formylbenzylacetate (semicarbazone, m. p. and mixed m. p. 169°) but also containing some ethyl phenylpyruvate in the last portion (colour with $FeCl_3$).

The ester prepared in this way therefore consists mainly of the $\beta\gamma$-form with a small amount of the $\alpha\beta$-isomeride.

trans-*α-Benzyl-γ-methyl-Δ^{β}-propene-αγ-dicarboxylic Acid.*—The above ester was hydrolysed by boiling for 2 days with 10 vols. of 10% HCl aq.; the *acid* formed fine needles, m. p. 184—185°, from H_2O (Found: C, 66·8; H, 5·8; *M*, dibasic, 234. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%; *M*, 234·1). The same acid was also formed on hydrolysis with 10% aq.-alc. KOH; it can also be recrystallised from C_6H_6 or AcOEt–petroleum.

It was recovered unchanged after boiling for 5 hrs. with 10 times its wt. of AcCl or with AcCl containing 20% $POCl_3$.

Oxidation. This was carried out as described on p. 2441. Ph·CHO was isolated in quantity; no methylmalonic or propionic acid could be detected, but pyruvic acid was indicated by qualitative tests, although a solid derivative was not isolated.

Ethyl trans-*α-Benzyl-γ-methyl-Δ^{β}-propene-αγ-dicarboxylate* (VIII).—The acid was esterified through the Ag salt; the ester had b. p. 195—196°/15 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0690, $n_{D}^{20\cdot0^\circ}$ 1·5070, $[R_L]_D$ 80·78.

Ozonisation. 9 G. of the ester were ozonised and the following fractions were obtained from the neutral portion at 16 mm.: (1) below 70°, about 2 g., consisting only of ethyl pyruvate (semicarbazone, m. p. and mixed m. p. 206°), giving no colour with $FeCl_3$. (2)135—150°, 6 g., which gave an intense purple-red colour with $FeCl_3$ and consisted of ethyl formylbenzylacetate (semicarbazone, m. p. and mixed m. p. 169°). No acid products were formed in this oxidation.

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