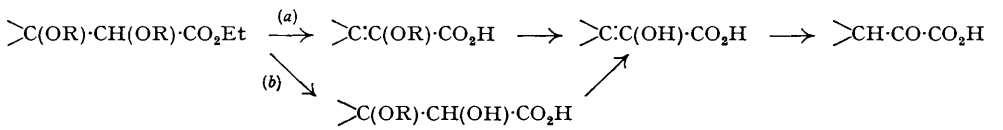
244. *Elimination Reactions of Esters. Part II.* The Formation of α-Keto-acids from Derivatives of αβ-Dihydroxy-acids, and Related Reactions.*

By R. P. Linstead, L. N. Owen, and R. F. Webb.

The action of alkali on αβ-diacyloxy-butyric and -β-phenylpropionic esters has been studied. The diacetates undergo normal hydrolysis, without elimination, but the dimethanesulphonates and ditoluene-*p*-sulphonates on mild treatment give the α-sulphonyloxy-crotonic or -cinnamic acids, by preferential elimination from the β-position. These products, on further alkaline hydrolysis, yield the corresponding α-keto-acids. The *erythro*- and the *threo*-forms of the αβ-disulphonyloxybutyrates give stereoisomeric α-sulphonyloxycrotonic acids, but only one α-sulphonyloxycinnamic acid is obtained from a pair of stereoisomeric β-phenyl-αβ-disulphonyloxypropionates.

Reaction of the disulphonates with sodium iodide yields crotonic or cinnamic acid by *cis*-elimination, *erythro*- *and threo*-disulphonates giving *cis*- and *trans*-products, respectively.

In the preceding paper it was shown that certain derivatives, $>C(OR)\cdot CH_2\cdot CO_2Et$, of β-hydroxy-esters, in which the hydroxyl group was itself esterified, underwent elimination on alkaline hydrolysis to yield the αβ-unsaturated acid $>C{:}CH\cdot CO_2H$, the yield of which was greatest when R was methanesulphonyl, toluene-*p*-sulphonyl, or nitro. The present communication is concerned with similar investigations on derivatives of αβ-dihydroxy-esters, which, since elimination would be expected to occur preferentially from the β-position, were expected to yield α-keto-acids through their enols [route (*a*)]:



This was confirmed, and evidence was also obtained to show that the reaction did not proceed by the less likely route (*b*).

Methyl *erythro*-αβ-dihydroxybutyrate, treated in pyridine with acetic anhydride, methanesulphonyl chloride, and toluene-*p*-sulphonyl chloride, severally, gave the liquid diacetate, and the solid disulphonates (III).† An alternative method for the ditoluene-*p*-sulphonate (III) involved conversion of crotonic acid *via* the chlorohydrin into the *threo*-epoxide, the methyl ester (I) of which was treated with toluene-*p*-sulphonic acid to give an oily monohydroxy-monotoluene-*p*-sulphonate. It was not established whether ring-fission had occurred exclusively in one direction, though from analogy with the corre-

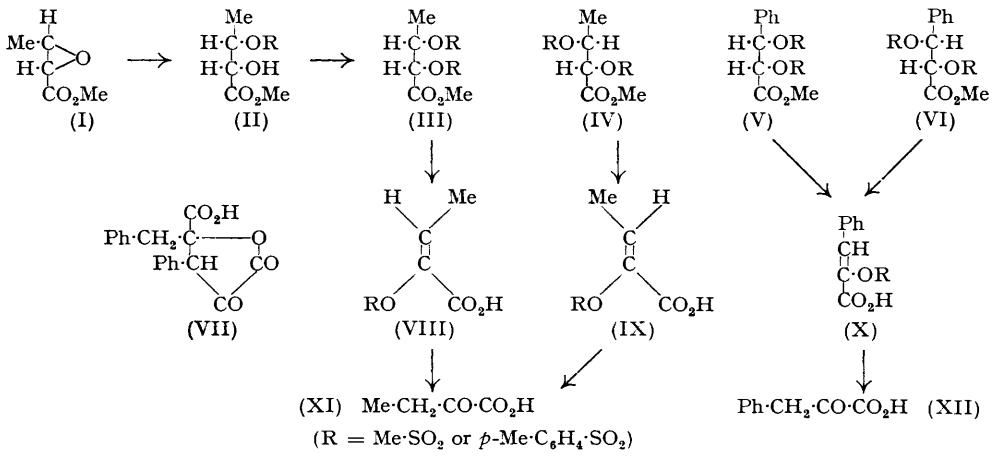
* Part I, preceding paper.

† Formulæ (I—VI) and (XIII—XV) represent, of course, optically active forms; the actual compounds used in this work were racemic.

sponding reaction of phenylglycidic acid (see below) the product was probably mainly the β-sulphonate (II); further reaction with toluene-*p*-sulphonyl chloride gave the *erythro*-ditoluene-*p*-sulphonate (III), this stereochemical result being in accordance with the occurrence of the usual inversion during the fission of an epoxide.

Methyl *threo*-αβ-dihydroxybutyrate was obtained by *cis*-hydroxylation of methyl crotonate with buffered aqueous permanganate at low temperature; it gave the solid disulphonates (IV).

Hydrolysis of the *erythro*-diacetate with concentrated aqueous-alcoholic alkali gave only the *erythro*-dihydroxy-acid; no keto-acid could be detected. The four sulphonates (III) and (IV), however, all gave α-ketobutyric acid (XI), and by the use of cold dilute alkali it was possible to stop the reaction at the intermediate stage; each disulphonate then gave a different crystalline unsaturated monosulphonate, all of which on further alkaline hydrolysis gave (XI), thus proving that the monosulphonates were α-substituted crotonic acids and confirming the expected preferential elimination of the β-substituent in an αβ-disulphonyloxy-ester. It seems likely that a bimolecular mechanism is involved, since a unimolecular process, involving an intermediate carbonium ion, would probably not result in the formation of a different monosulphonate from each disulphonate. Furthermore, on the assumption that *trans*-elimination occurs, an *erythro*- and a *threo*-disulphonate

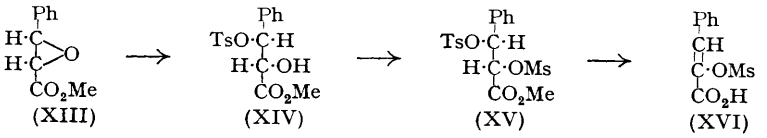


will give respectively a *cis*- and a *trans*-α-sulphonyloxycrotonic acid. The *cis*-configuration (VIII) can therefore be allocated to the methanesulphonate, m. p. 112—113°, and the toluene-*p*-sulphonate, m. p. 118°, derived from the *erythro*-esters (III); and the *trans*-configuration (IX) to the methanesulphonate, m. p. 94—95°, and the toluene-*p*-sulphonate, m. p. 138°, from (IV).

From the *erythro*- and the *threo*-isomer of methyl αβ-dihydroxy-β-phenylpropionate, with the appropriate acid chloride in pyridine, the four crystalline disulphonates (V) and (VI) were obtained. Alkaline hydrolysis of the diacetyl and the dibenzoyl derivative of *threo*-αβ-dihydroxy-β-phenylpropionic acid gave only the *threo*-dihydroxy-acid, but the sulphonates again underwent elimination. In this series, however, an interesting difference from the behaviour of the dihydroxybutyric derivatives was observed, in that the same unsaturated monosulphonate (X) was formed from each of the corresponding disulphonates (V) and (VI); further alkaline hydrolysis of the monomethane- and mono-toluene-*p*-sulphonate gave phenylpyruvic acid (XII), and reaction of methyl phenylpyruvate with toluene-*p*-sulphonyl chloride in pyridine gave methyl α-toluene-*p*-sulphonyloxycinnamate, identical with the product obtained by treatment of the toluene-*p*-sulphonate (X) with diazomethane. This established the structures of (X), though in this series the configurations, which are probably *trans*, clearly cannot be deduced from those of their precursors, and the mechanism of elimination may differ from that in the dihydroxybutyric series. When the disulphonates (VI) were hydrolysed with concentrated methanolic potassium

hydroxide a weakly acidic product was obtained which, when separated from polymer, was identified as the " di(phenylpyruvic) acid " (VII) described by Jarrousse (*Ann. Chim.*, 1938, **9**, 157).

Reaction of methyl αβ-epoxy-β-phenylpropionate (prepared by the Darzens condensation of benzaldehyde with methyl chloroacetate) with toluene-*p*-sulphonic acid gave a crystalline monohydroxy-monotoluene-*p*-sulphonate which was shown to be (XIV) from the following observations. Toluene-*p*-sulphonation gave the *threo*-ditoluene-*p*-sulphonate (VI; R = *p*-Me·C_6H_4·SO_2), thus establishing the configuration, whilst methanesulphonation gave a methanesulphonate–toluene-*p*-sulphonate which on reaction with alkali furnished the α-methanesulphonyloxycinnamic acid (XVI); the mixed derivative must therefore be (XV) and hence the monotoluene-*p*-sulphonate is the β-derivative (XIV). It follows, from the *threo*-configuration of (XIV), that the epoxide must have been mainly the *erythro*-form (XIII).



(Ms = Me·SO_2; Ts = *p*-Me·C_6H_4·SO_2)

In view of the general similarity between the reactions of sulphonyl esters and those of halides, it is interesting to compare some of the reactions described above with those of the corresponding bromo-acids. It is well established that reaction of *erythro*-αβ-dibromobutyric acid, or its esters, with aqueous or alcoholic alkali, gives almost entirely *cis*-α-bromocrotonic acid (*inter al.*, James, *J.*, 1910, **97**, 1572); the *threo*-dibromo-acid is reported to give a mixture of *cis*- and *trans*-β-bromocrotonic acid (Michael and Schulthess, *J. pr. Chem.*, 1892, **46**, 263), but further confirmation is desirable. With the αβ-dibromo-β-phenylpropionic acids and esters the composition of the product is greatly influenced by the nature of the reaction medium, but it is of interest that the stereoisomeric methyl esters, on treatment with alcoholic alkali, give mainly the same *trans*-α-bromocinnamic acid (Sudborough and Thompson, *J.*, 1903, **83**, 666; James and Sudborough, *J.*, 1909, **95**, 1541). Broadly, therefore, in both series, the reactions are similar to those shown in the first stage of the hydrolysis of the sulphonates. In the second stage, however, there are some important points of difference, because, although *cis*- or *trans*-α-bromocrotonic acid on further reaction with aqueous alkali behaves like the corresponding α-sulphonate and gives α-ketobutyric acid (Owen, *J.*, 1945, 385), the α-bromocinnamic acids do not give phenylpyruvic acid but undergo further elimination to yield phenylpropiolic acid. Strong evidence has been presented that substitution of the halogen in αβ-unsaturated α-bromo-acids not does occur directly, but only after an initial prototropic change (Owen and Sultanbawa, *J.*, 1949, 3089), and the behaviour of α-bromocinnamic acid, which cannot undergo the initial isomerisation, is therefore understandable (see also Newman and Owen, *J.*, 1952, 4722). The formation of phenylpyruvic acid from the α-sulphonyloxycinnamic acids therefore suggests the operation of a mechanism different from that postulated for the bromo-acids. In the hydrolysis of a halide, the breaking of the carbon–halogen bond corresponds to the " alkyl–oxygen " fission of an ester, and is of course the only type possible. Now although esters of sulphonic acids usually undergo this form of fission (which explains why their reactions are often similar to those of halides), it seems likely that in circumstances where " alkyl–oxygen " fission is inhibited the " acyl–oxygen " type R–O–¦–Ts may operate (cf. Ferns and Lapworth, *J.*, 1912, **101**, 273). This would explain why the reactions of the disulphonates (VI) with methanolic potassium hydroxide gave only phenylpyruvic acid and no α-methoxycinnamic acid.

The availability of the sulphonyl derivatives of the αβ-dihydroxy-butyric and -β-phenylpropionic esters led us to examine their behaviour towards sodium iodide, since with this reagent a compound containing sulphonyloxy-groups attached to two vicinal carbon atoms, one of which is primary, *e.g.*, R·CH(OTs)·CH_2·OTs, gives the unsaturated product R·CH:CH_2 (cf. Bladon and Owen, *J.*, 1950, 598; Foster and Overend, *J.*, 1951,

3452) whereas if both groups are secondary they are usually resistant to such treatment (for examples, see Bell and Synge, *J.*, **1937**, 1711; Bacon, Bell, and Lorber, *J.*, **1940**, 1147). The dimethanesulphonates (III), (IV), (V), and (VI), however, all reacted slowly with sodium iodide in boiling acetone to give methyl *cis*-crotonate, methyl *trans*-crotonate, methyl *cis*-cinnamate, and methyl *trans*-cinnamate, respectively. These stereochemical results are of much interest, in that the *erythro*- and *threo*-esters give *cis*- and *trans*-products respectively, *i.e.*, the overall result is one of *cis*-elimination. This is the opposite to the debromination of dibromides with potassium iodide (cf. Crombie, *Quart. Reviews*, 1952, **6**, 101); thus *erythro*-αβ-dibromo-butyric and -β-phenylpropionic acids give *trans*-crotonic and *trans*-cinnamic acid, respectively (Erlenmeyer and Müller, *Ber.*, 1882, **15**, 49; van Duin, *Rec. Trav. chim.*, 1926, **45**, 347). The reaction is being studied in more detail, and, if of more general application, may provide a valuable method for changing the configuration of double bonds by the sequence :

$$\textit{trans}\text{-Olefin} \xrightarrow[\text{Hydroxylation}]{\textit{trans}\text{-}} \textit{cis}\text{-Diol} \longrightarrow \textit{cis}\text{-Disulphonate} \longrightarrow \textit{cis}\text{-Olefin}$$

Experimental

Methyl erythro-αβ-*Dihydroxybutyrate.*—*erythro*-αβ-Dihydroxybutyric acid, m. p. 82—83°, prepared by catalytic hydroxylation of crotonic acid with aqueous pertungstic acid at 70° (Mugdan and Young, *J.*, 1949, 2999), was treated in methanol with excess of ethereal diazomethane. Removal of solvent under reduced pressure gave the methyl ester, which was used without further purification.

Methyl threo-αβ-*Dihydroxybutyrate.*—To methyl crotonate (66·5 g.) in ethanol (3 l.) at −40°, a solution of potassium permanganate (127 g.) and magnesium sulphate heptahydrate (100 g.) in water (4 l.) was added with vigorous stirring during 5 hours. The mixture was then allowed to attain room temperature, and the filtered solution was concentrated (to 2 l.) and continuously extracted with ether; evaporation of the dried extracts gave the methyl ester (14 g.).

Methyl αβ-*Epoxybutyrate.*—β-Methylglycidic acid (5 g.), m. p. 88° (Braun, *J. Amer. Chem. Soc.*, 1930, **52**, 3185), with an excess of ethereal diazomethane afforded the *methyl* ester (4·9 g.), b. p. 160—161°, n_D^{18} 1·4205 (Found : C, 51·5; H, 7·0. $C_5H_8O_3$ requires C, 51·7; H, 7·0%).

Derivatives of Methyl erythro-αβ-*Dihydroxybutyrate.*—(i) The ester (1·1 g.), acetic anhydride (2·4 c.c.), and pyridine (6 c.c.) were kept at 0° for 12 hours. The solution was then diluted with ice-water and extracted with chloroform, the extract washed with 2N-sulphuric acid, and with water, dried, and evaporated, and the residue distilled, affording *methyl* erythro-αβ-*diacetoxybutyrate* (0·75 g.), b. p. 85°/0·01 mm., n_D^{20} 1·4289 (Found : C, 49·7; H, 6·6. $C_9H_{14}O_6$ requires C, 49·5; H, 6·5%).

(ii) The ester (6·7 g.) in pyridine (25 c.c.) was cooled to −5°, and toluene-*p*-sulphonyl chloride (20 g.) in pyridine (90 c.c.) was added during 1½ hours. After 16 hours at 0° ice-water (230 c.c.) was added, and the product was isolated by chloroform extraction as described for the diacetate. It was an oil which on trituration with methanol slowly deposited crystals (9·45 g.), m. p. 59—63°. Recrystallisation from an equal volume of methanol gave *methyl* erythro-αβ-*ditoluene*-p-*sulphonyloxybutyrate*, m. p. 73° (Found : C, 51·9; H, 5·2; S, 14·5. $C_{19}H_{22}O_8S_2$ requires C, 51·6; H, 5·0; S, 14·5%).

(iii) Similar treatment of the ester (13·3 g.) in pyridine (20 c.c.) with methanesulphonyl chloride (18 c.c.) in pyridine (80 c.c.) gave needles (18·1 g.) (from methanol) of *methyl* erythro-αβ-*dimethanesulphonyloxybutyrate*, m. p. 63—64° (Found : C, 29·3; H, 4·9; S, 22·1. $C_7H_{14}O_8S_2$ requires C, 29·0; H, 4·9; S, 22·1%).

Derivatives of Methyl threo-αβ-*Dihydroxybutyrate.*—Prepared as described for the *erythro*-isomers, the *ditoluene*-p-*sulphonate* formed needles (from methanol), m. p. 90° (Found : C, 51·1; H, 5·0; S, 14·3%), and the *dimethanesulphonate* needles (from methanol), m. p. 128° (Found : C, 29·1; H, 4·8; S, 21·9%).

Reaction of Methyl αβ-*Epoxybutyrate with Toluene*-p-*sulphonic Acid.*—A solution of the ester (2·3 g.) and toluene-*p*-sulphonic acid (3·5 g.) in dry ether was set aside at room temperature overnight and then evaporated to an oil. A portion (0·3 g.), on treatment with toluene-*p*-sulphonyl chloride in pyridine, gave a solid (0·2 g.), which when recrystallised from methanol afforded methyl *erythro*-αβ-ditoluene-*p*-sulphonyloxybutyrate, m. p. and mixed m. p. 73°.

Alkaline Hydrolysis of Methyl erythro-αβ-*Diacetoxybutyrate.*—A solution of the ester (1 g.) and potassium hydroxide (1 g.) in water (3 c.c.) and ethanol (12 c.c.) was boiled under reflux

for 2 hours, then cooled and passed through a cation-exchange column (" Amberlite "). Elution with ethanol, and evaporation, gave a syrup which gave no ketonic reactions and slowly crystallised to give *erythro*-αβ-dihydroxybutyric acid (0·3 g.), m. p. and mixed m. p. 81—82° (from ethyl acetate). The alcoholic distillate, also, was free from ketonic material.

Reactions of the Methyl αβ-Disulphonyloxybutyrates with Aqueous Alkali.—(i) The *erythro*-ditoluene-*p*-sulphonate (4·1 g.) in dioxan (75 c.c.) was added to potassium hydroxide (3·4 g.) in water (25 c.c.); the mixture was vigorously stirred for 18 hours at room temperature, diluted with water (100 c.c.), and then neutralised with carbon dioxide. The dioxan was removed below 50°, and the aqueous solution acidified with hydrochloric acid and extracted with ether (3 × 60 c.c.). Evaporation of the dried (Na_2SO_4) extracts gave cis-α-*toluene*-p-*sulphonyloxycrotonic acid* (2·2 g.), which crystallised from carbon tetrachloride in rosettes of needles, m. p. 118° (Found: C, 51·7; H, 4·8; S, 12·6. $C_{11}H_{12}O_5S$ requires C, 51·6; H, 4·7; S, 12·5%).

(ii) The *erythro*-dimethanesulphonate (11·6 g.) in dioxan (250 c.c.) with potassium hydroxide (7·0 g.) in water (150 c.c.) similarly gave cis-α-*methanesulphonyloxycrotonic acid* (2·9 g.) which crystallised from chloroform–carbon tetrachloride in needles, m. p. 112—113° (Found: C, 33·5; H, 4·4; S, 17·5. $C_5H_8O_5S$ requires C, 33·4; H, 4·5; S, 17·8%).

The acidic aqueous residue was continuously extracted with ether for 48 hours, and the extract dried ($MgSO_4$) and evaporated to an oil (2·2 g.), mainly α-ketobutyric acid. A portion (0·2 g.) with excess of aqueous 2 : 4-dinitrophenylhydrazine sulphate gave a yellow precipitate (0·4 g.) which when recrystallised from aqueous ethanol gave the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 195°.

(iii) The *threo*-ditoluene-*p*-sulphonate (8·2 g.) with potassium hydroxide (6·8 g.), water (50 c.c.), and dioxan (150 c.c.) gave trans-α-*toluene*-p-*sulphonyloxycrotonic acid* (2·4 g.), m. p. 138° (from benzene) (depressed to 104—113° on admixture with the isomer of m. p. 118°) (Found: C, 51·8; H, 4·8; S, 13·0%), and α-ketobutyric acid (1·9 g.).

(iv) The *threo*-dimethanesulphonate (8·7 g.) with potassium hydroxide (5·0 g.) in water (37 c.c.) and dioxan (180 c.c.) gave trans-α-*methanesulphonyloxycrotonic acid* (4·2 g.), which crystallised from benzene in needles, m. p. 94—95° (depressed to 83—86° on admixture with the isomer of m. p. 112—113°) (Found: C, 33·2; H, 4·6; S, 17·1%).

Reactions of the α-Sulphonyloxycrotonic Acids with Aqueous Alkali.—*cis*-α-Methanesulphonyloxycrotonic acid (0·18 g.) was boiled under reflux for 1 hour with N-sodium hydroxide (2 c.c.). The cooled solution was diluted with water (20 c.c.) and 2N-sulphuric acid (4 c.c.), and a standard solution (15 c.c.) of 2 : 4-dinitrophenylhydrazine sulphate was added (1·5 g. of base in 200 c.c. of concentrated sulphuric acid diluted to 1 l. with water). The yellow precipitate (0·14 g.) was collected, washed with 2N-sulphuric acid and with water, and dried at 100°. Crystallisation from aqueous ethanol afforded the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 195°, of α-ketobutyric acid.

trans-α-Methanesulphonyloxycrotonic acid (0·18 g.), and the *cis*- and the *trans*-α-toluene-*p*-sulphonyloxycrotonic acid (0·26 g. each), on similar treatment all gave the 2 : 4-dinitrophenylhydrazone, m. p. 195° (yields, 0·14, 0·21, and 0·16 g., respectively).

Methyl erythro-αβ-*Dihydroxy*-β-*phenylpropionate.*—Treatment of the dihydroxy-acid, m. p. 121° (Böeseken, *Rec. Trav. chim.*, 1922, **41**, 206) with ethereal diazomethane gave the methyl ester, m. p. 87° (from carbon tetrachloride).

Methyl threo-αβ-*Dihydroxy*-β-*phenylpropionate.*—Methyl cinnamate (80 g.) in ethanol (6 l.) was oxidised at −40° by addition of potassium permanganate (96 g.) and magnesium sulphate heptahydrate (100 g.), in water (3 l.). The mixture was worked up as described for the oxidation of methyl crotonate, and gave the *threo*-dihydroxy-ester, which crystallised from carbon tetrachloride in needles (68 g.), m. p. 69°.

Derivatives of Methyl erythro- *and* threo-αβ-*Dihydroxy*-β-*phenylpropionate.*—Treatment of the esters with the appropriate acid chloride in pyridine at 0°, as described for the dihydroxybutyric derivatives, gave solid products on dilution of the reaction mixtures with ice-water. Recrystallisation (from methanol in each case) gave the erythro-*ditoluene*-p-*sulphonate*, m. p. 132° (Found: C, 57·3; H, 4·8; S, 12·5. $C_{24}H_{24}O_8S_2$ requires C, 57·1, H, 4·8; S, 12·7%); the threo-*ditoluene*-p-*sulphonate*, m. p. 132° (Found: C, 57·0; H, 4·7; S, 12·4%) (depressed to *ca.* 120° on admixture with the *erythro*-isomer); the erythro-*dimethanesulphonate*, m. p. 118—119° (Found: C, 41·1; H, 4·6; S, 18·1. $C_{12}H_{16}O_8S_2$ requires C, 40·9; H, 4·6; S, 18·2%); and the threo-*dimethanesulphonate*, m. p. 110° (Found: C, 40·9; H, 4·6; S, 18·2%).

Methyl αβ-*Epoxy*-β-*phenylpropionate.*—Benzaldehyde (106 g.) and methyl chloroacetate (109 g.) in benzene (200 c.c.) were cooled in ice–salt, and dry, powdered sodium methoxide (70 g.) was added, with vigorous stirring, during 4 hours. Stirring was then maintained for

16 hours at room temperature and the product was poured on crushed ice (1 kg.), and acidified with 2N-acetic acid (650 c.c.). The benzene layer was washed successively with 2N-acetic acid, water, 10% aqueous sodium carbonate, and water, then dried (Na_2SO_4) and evaporated. Distillation of the residue gave crude methyl αβ-epoxy-β-phenylpropionate (110 g.), b. p. 100—110°/0·6 mm., n_D^{15} 1·5333, which could not be further purified by distillation (Found: C, 64·5; H, 5·6. Calc. for $C_{10}H_{10}O_3$: C, 67·4; H, 5·7%).

Methyl threo-α-*Hydroxy*-β-*phenyl*-β-*toluene*-p-*sulphonyloxypropionate*.—A solution of crude methyl αβ-epoxy-β-phenylpropionate (4·45 g.) and anhydrous toluene-*p*-sulphonic acid (4·7 g.) in dry ether (60 c.c.) was boiled under reflux for 15 min. and set aside at room temperature for 12 hours. The crystalline *ester* (3·5 g.) was washed with ether (20 c.c.) and recrystallised from carbon tetrachloride as colourless needles, m. p. 92°, which rapidly became brown on storage (Found: C, 57·7; H, 5·3; S, 9·1. $C_{17}H_{18}O_6S$ requires C, 58·3; H, 5·2; S, 9·2%). Treatment with toluene-*p*-sulphonyl chloride in pyridine afforded the *threo*-ditoluene-*p*-sulphonate, m. p. and mixed m. p. 132°. Acetylation (acetic anhydride in pyridine) afforded the threo-α-*acetate* β-*toluene*-p-*sulphonate* (needles), m. p. 83° (Found: C, 57·9; H, 5·2; S, 8·3. $C_{19}H_{20}O_7S$ requires C, 58·3; H, 5·1; S, 8·1%); treatment with methanesulphonyl chloride gave the threo-α-*methanesulphonate* β-*toluene*-p-*sulphonate* (needles), m. p. 111° (Found: C, 49·3; H, 4·7; S, 15·7. $C_{18}H_{20}O_8S_2$ requires C, 49·0; H, 4·7; S, 15·5%).

Reactions of the threo-αβ-*Diacyloxy*-β-*phenylpropionic Acids with Aqueous Alkali*.—(i) The diacetoxy-acid (4·0 g.) (Dieckmann, *Ber.*, 1910, **43**, 1035) with potassium hydroxide (14 g.) in water (50 c.c.) for 3 hours at 20° gave only *threo*-αβ-dihydroxy-β-phenylpropionic acid (1·95 g., 71%), m. p. and mixed m. p. 141°.

(ii) The dibenzoyloxy-acid (3·4 g.) (Mayer, *Ber.*, 1897, **30**, 1612) with potassium hydroxide (1·4 g.) in water (50 c.c.) for 12 hours at 20° gave only benzoic acid (0·97 g.) and the dihydroxy-acid (1·32 g., 83%), m. p. and mixed m. p. 141°.

Reactions of the Methyl threo-β-*Phenyl*-αβ-*disulphonyloxypropionates with Methanolic Alkali*.—(i) The ditoluene-*p*-sulphonate (10·9 g.) was shaken for 16 hours with potassium hydroxide (16·8 g.) in methanol (150 c.c.); the precipitated potassium toluene-*p*-sulphonate (8·4 g., 100%) was then removed. The solution was acidified with concentrated hydrochloric acid, and the precipitated potassium chloride filtered off and washed with methanol (10 c.c.). The combined filtrate and washings were diluted to 400 c.c. with water, concentrated under reduced pressure below 50° to 150 c.c., and extracted with ether (3 × 80 c.c.). Evaporation of the dried (Na_2SO_4) extracts gave a solid (3·9 g.), m. p. 165—170° (decomp.), which was freed from polymer by repeated precipitation with benzene from chloroform, to give fibrous filaments of " di(phenylpyruvic) acid," m. p. 172—173° (decomp.) (Found: C, 69·3; H, 4·6. Calc. for $C_{18}H_{14}O_6$: C, 69·7; H, 4·5%) (Jarrousse, *loc. cit.*, gives m. p. *ca.* 200°).

(ii) The dimethanesulphonate (7·4 g.), when similarly treated with potassium hydroxide (16·8 g.) in methanol (150 c.c.), gave potassium methanesulphonate (4·9 g.) and " di(phenylpyruvic) acid " (1·3 g.), m. p. 172—173° (decomp.).

Reactions of the Methyl β-*Phenyl*-αβ-*disulphonyloxypropionates with Aqueous Alkali*.—(i) The *threo*-ditoluene-*p*-sulphonate (10·1 g.) in dioxan (150 c.c.) was added to potassium hydroxide (6·8 g.) in water (50 c.c.), and the mixture shaken for 16 hours, diluted with water (150 c.c.), and neutralised with carbon dioxide. The dioxan was removed under reduced pressure, and the aqueous solution was extracted with ether (50 c.c.) to yield an oil (0·2 g.); on trituration with methanol this deposited a solid (0·13 g.) which crystallised from methanol in plates, m. p. 82°.

The aqueous solution was acidified with concentrated hydrochloric acid and extracted with ether (3 × 300 c.c.), to give α-*toluene*-p-*sulphonyloxycinnamic acid* (3·5 g.), m. p. 165° (from ethylene dichloride) (Found: C, 60·6; H, 4·7; S, 10·2. $C_{16}H_{14}O_5S$ requires C, 60·4; H, 4·4; S, 10·1%). Treatment of a portion with ethereal diazomethane afforded the *methyl* ester, which crystallised from methanol in plates, m. p. 83° (Found: C, 61·3; H, 5·0; S, 9·7. $C_{17}H_{16}O_5S$ requires C, 61·4; H, 4·9; S, 9·6%), identical with the solid obtained from the neutral fraction.

(ii) The *erythro*-ditoluene-*p*-sulphonate (5·0 g.) under the same conditions gave the same α-toluene-*p*-sulphonyloxycinnamic acid (1·6 g.), m. p. and mixed m. p. 165°; the methyl ester had m. p. and mixed m. p. 83°.

(iii) The *threo*-dimethanesulphonate (3·5 g.) in dioxan (75 c.c.), with potassium hydroxide (3·4 g.) in water (25 c.c.) similarly gave α-*methanesulphonyloxycinnamic acid* (1·9 g.), needles (from chloroform), m. p. 153° (Found: C, 49·2; H, 4·2; S, 13·3. $C_{10}H_{10}O_5S$ requires C, 49·6; H, 4·2; S, 13·2%). Treatment with diazomethane gave the *methyl* ester, m. p. 93° (from methanol) (Found: C, 51·6; H, 4·8; S, 12·8. $C_{11}H_{12}O_5S$ requires C, 51·6; H, 4·7; S, 12·5%).

(iv) The *erythro*-dimethanesulphonate (3·5 g.) gave the same α-methanesulphonyloxycinnamic acid (1·7 g.), m. p. and mixed m. p. 153°.

(v) Methyl *threo*-α-methanesulphonyloxy-β-phenyl-β-toluene-*p*-sulphonyloxypropionate (0·39 g.) in dioxan (7·5 c.c.), with potassium hydroxide (0·34 g.) in water (2·5 c.c.), afforded α-methanesulphonyloxycinnamic acid (0·21 g.), m. p. 141—144°; recrystallisation from chloroform gave needles, m. p. and mixed m. p. 153°. The methyl ester had m. p. and mixed m. p. 93°.

*Methyl α-Toluene-*p*-sulphonyloxycinnamate from Methyl β-Phenylpyruvate.*—β-Phenylpyruvic acid (0·82 g.), m. p. 150—154° (*Org. Synth.*, Coll. Vol. 2, p. 519) was treated with ethereal diazomethane, and the ester obtained on evaporation was dissolved in pyridine (10 c.c.) and cooled to −5°. Toluene-*p*-sulphonyl chloride (1·0 g.) was added, and after 16 hours at 0° the solution was diluted with ice-water (20 c.c.). The precipitated oil was extracted with chloroform (4 × 4 c.c.), washed with 20% aqueous sulphuric acid, then with water, and dried (Na_2SO_4). The solvent was evaporated, and the residual oil (0·5 g.) on trituration with methanol deposited a solid (0·19 g.), m. p. 74—78°; recrystallisation from methanol afforded methyl α-toluene-*p*-sulphonyloxycinnamate, m. p. and mixed m. p. 82°.

Reactions of α-Sulphonyloxycinnamic Acids with Aqueous Alkali.—α-Toluene-*p*-sulphonyloxycinnamic acid (0·2 g.) was boiled under reflux for 1 hour with potassium hydroxide (0·18 g.) in water (10 c.c.), and the cooled solution was acidified with hydrochloric acid and extracted with ether (3 × 5 c.c.), to give a solid (0·1 g.), m. p. 120—131°. Recrystallisation from chloroform afforded phenylpyruvic acid, m. p. 145°.

α-Methanesulphonyloxycinnamic acid (0·26 g.), similarly treated, gave phenylpyruvic acid (0·14 g.), m. p. 146°.

*Reactions of the αβ-Dimethanesulphonyloxy-esters with Sodium Iodide.**—(i) Methyl *threo*-αβ-dimethanesulphonyloxy-β-phenylpropionate (2·54 g.) and sodium iodide dihydrate (5·0 g.) in acetone (300 c.c.) were refluxed for 49 hours; the precipitated double salt of sodium methanesulphonate and sodium iodide (1·21 g.) was removed and the filtrate evaporated under reduced pressure. Water (20 c.c.) and chloroform (100 c.c.) were added, the iodine was removed by means of a saturated solution of sodium thiosulphate, and the chloroform layer separated, dried (Na_2SO_4), and evaporated. The semi-solid residue was dissolved in methanol (4 c.c.), then cooled, and the unchanged dimethanesulphonate which crystallised (0·83 g.) was filtered off; addition of light petroleum (b. p. 40—60°) to the filtrate precipitated a further quantity (0·12 g.). The filtrate was evaporated, water (35 c.c.) added, and the mixture distilled in steam. The steam-volatile methyl cinnamate (0·45 g.) was collected and after recrystallisation from light petroleum (b. p. 40—60°) had m. p. and mixed m. p. 36°.

(ii) Methyl *erythro*-αβ-dimethanesulphonyloxy-β-phenylpropionate (2·0 g.) and sodium iodide dihydrate (4 g.) in acetone (50 c.c.) when refluxed for 34 hours gave the sodium methanesulphonate–sodium iodide double salt (1·3 g.) and a steam-volatile ester (0·54 g.), b. p. 124—125°/16 mm. This was identified as methyl *cis*-cinnamate by *cis*-hydroxylation, and by hydrolysis, as follows: The ester (0·3 g.) in ethanol (20 c.c.) at −30° was treated with potassium permanganate (0·35 g.) and magnesium sulphate heptahydrate (0·35 g.) in water (11 c.c.) and gave methyl *erythro*-αβ-dihydroxy-β-phenylpropionate (0·14 g.), m. p. and mixed m. p. 87°. The unsaturated ester (0·2 g.) when hydrolysed gave *cis*-cinnamic acid (0·13 g.), m. p. 42°.

(iii) Methyl *erythro*-αβ-dimethanesulphonyloxybutyrate (2·0 g.) and sodium iodide dihydrate (4·0 g.) in acetone (50 c.c.) were refluxed for 28 hours; the double salt (1·82 g.) was filtered off and the filtrate evaporated under reduced pressure. Water (2 c.c.) and a saturated solution of sodium thiosulphate (3 c.c.) were added, the mixture was extracted with ether (4 × 6 c.c.), and the extract dried (Na_2SO_4) and evaporated. The residue (0·4 g.) was hydrolysed at room temperature with aqueous alcoholic (1 : 1) 0·5N-potassium hydroxide (10 c.c.) and gave a liquid unsaturated acid, b. p. 169° (0·1 g.) (*cis*-crotonic acid has b. p. 169°). This was re-esterified and treated with methanolic ammonia for several days at 0°. Evaporation, and recrystallisation of the residue from water, gave *cis*-crotonamide, m. p. 100—101° (lit., 102°), depressed to 94—97° on admixture with *trans*-crotonamide.

(iv) Methyl *threo*-αβ-dimethanesulphonyloxybutyrate (2·0 g.) when refluxed with sodium iodide dihydrate (4·0 g.) in acetone (50 c.c.) gave an ester (0·4 g.), b. p. 116°, which on hydrolysis afforded *trans*-crotonic acid (0·2 g.), m. p. and mixed m. p. 73°.

DEPARTMENT OF ORGANIC CHEMISTRY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7.

[*Received, December 17th*, 1952.]

* These reactions were carried out with exclusion of light.