LXXVII.—*The Action of Tribromopropane on the Sodium Derivative of Ethyl Malonate. Part II. Formation of $\Delta^{\alpha\zeta}$ -Heptadi-inene- δ -carboxylic Acid (ψ -m-Toluic Acid), $(\text{CH}:\text{C}\cdot\text{CH}_2)_2\text{C}(\text{CO}_2\text{H})_2$.*

By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN
(Schunck Research Fellow in the University of Manchester).

THE principal product of the action of tribromopropane on the sodium derivative of ethyl malonate is *ethyl γ -bromoallylmalonate*, a detailed account of which is given in the preceding communication, and it is there stated that besides this substance, another bromo-ester (b. p. $191^\circ/11$ mm.) is always produced in considerable quantities. Investigation has shown that this bromo-ester is *ethyl $\gamma\gamma$ -dibromodiallylmalonate*, produced according to the equation

When this ester is digested with alcoholic potash, it is decomposed with elimination of hydrogen bromide and formation of $\Delta^{\alpha\zeta}$ -heptadi-inene- δ -carboxylic acid,

which crystallises in prisms and melts at 47° . This interesting acid, like $\Delta\gamma$ -butinene- α -carboxylic acid, $\text{CH}:\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (p. 827), of

which it is a derivative, evidently contains acetylene linkings, since it yields a copper derivative when its aqueous solution is mixed with ammoniacal cuprous chloride and the silver salt has an abnormal composition, the analytical numbers lying between those required by the formulæ $C_8H_7O_2Ag$, $AgOH$ and $2AgOH$.

The interest which attaches to this acid is due to the extraordinary ease with which it is converted into the isomeric *m*-toluic acid, and this remarkable intramolecular change led us in the first instance (Proc., 1906, 22, 134) to name the acid "*ψ*-*m*-toluic acid" and to assign to it the constitution

The conversion into *m*-toluic acid takes place when the acid is simply boiled with water or when it is treated in the cold with hydrobromic acid, but heat alone does not bring about this change.

The discovery that the acid yields a copper derivative and especially the study of the values obtained in the determination of the magnetic rotation of ethyl *ψ*-*m*-toluate (p. 845) caused us to discard the above formula, and there can now no longer be any doubt that the constitution of the acid is represented by the formula

ψ-*m*-Toluic acid is therefore somewhat closely allied to *isophenyl*-acetic acid,*

(Buchner, *Ber.*, 1898, 31, 987; Braren and Buchner, *Ber.*, 1891, 34, 987), and it is worthy of note that this acid when heated at 100° with a solution of hydrogen bromide in acetic acid is converted by intramolecular change into a derivative of *p*-toluic acid,

The only other somewhat similar cases which we have been able to find are the formation of tetramethyldihydrobenzene (euterpane) from dihydroeucarveol by the action first of phosphorus pentachloride and then of quinoline (Baeyer, *Ber.*, 1898, 31, 2077),

* For some time we were of opinion that *ψ*-*m*-toluic acid was identical with *α*-*isophenyl*acetic acid, and we are greatly indebted to Prof. Buchner for sending us a specimen of this valuable acid which enabled us to decide against the identity.

and the case of eucarvone, which when heated to boiling for an hour is quantitatively converted into carvacrol,

and when treated in the cold with phosphorus pentachloride yields 2-chlorocymene (Klages and Kraith, *Ber.*, 1899, 32, 2558).

In endeavouring to find an explanation of the remarkable ease with which ψ -*m*-toluic acid is converted into *m*-toluic acid, it should be borne in mind that the intramolecular change takes place rapidly when the acid is boiled with water or dilute acids, but is not brought about by heat alone (p. 843). If we assume that the water, which appears to be essential to the transformation, is added to the acetylenic linkings in ψ -*m*-toluic acid (in the way so frequently observed in other cases) and is then eliminated again, we obtain the following comparatively simple explanation of the conversion into *m*-toluic acid:

Ethyl $\gamma\gamma$ -Dibromodiallylmalonate, $(\text{CH}_2 \cdot \text{CBr} \cdot \text{CH}_2)_2 \text{C}(\text{CO}_2\text{Et})_2$, and its Conversion into $\Delta^{\alpha\epsilon}$ -Heptadi-inene- δ -carboxylic Acid (ψ -*m*-Toluic Acid), $(\text{CH} : \text{C} \cdot \text{CH}_2)_2 \text{C}(\text{CO}_2\text{H})_2$.

When tribromopropane reacts with the sodium derivative of ethyl malonate, under the conditions described in the preceding communication, an oil (*A*) of high boiling point is always obtained in considerable quantity (compare p. 821). This was twice fractionated under 11 mm. pressure, when almost the whole quantity distilled at about 191°:

0.2296 gave 0.3313 CO_2 and 0.0971 H_2O . C = 39.3; H = 4.7.

0.2434 „ 0.2310 AgBr. Br = 40.3.

$\text{C}_{13}\text{H}_{18}\text{O}_4\text{Br}_2$ requires C = 39.2; H = 4.5; Br = 40.2 per cent.

Ethyl $\gamma\gamma$ -dibromodiallylmalonate is a viscid, heavy oil, possessing a rather unpleasant odour, and is very slowly attacked by boiling with dilute sulphuric acid or with potassium carbonate. Its conversion into ψ -*m*-toluic acid was effected as follows.

The dibromo-ester (20 grams) was mixed with a strong solution of caustic potash (25 grams) in methyl alcohol, when a large quantity of sodium bromide immediately separated, and, after boiling for three

hours on the water-bath, the solution was diluted with water and evaporated until free from alcohol. After mixing with powdered ice, hydrochloric acid was added until the solution just reacted with congo-paper, and the oily precipitate was rapidly extracted three times with ether. The ethereal solution was dried over calcium chloride and evaporated, when an oil remained which, over sulphuric acid in a vacuum desiccator, gradually crystallised. The crystals were left in contact with porous porcelain until quite free from oil, and then recrystallised several times from light petroleum (b. p. 60—70°). Three different preparations were analysed :

0·1027 gave 0·2639 CO₂ and 0·0533 H₂O. C = 70·1 ; H = 5·8.

0·1837 „ 0·4670 CO₂ „ 0·0998 H₂O. C = 69·3 ; H = 6·0.

0·1459 „ 0·3726 CO₂ „ 0·0782 H₂O. C = 69·6 ; H = 6·0.

C₈H₈O₂ requires C = 70·5 ; H = 5·9 per cent.

$\Delta^{\alpha\zeta}$ -Heptadi-inene- δ -carboxylic acid (ψ -*m*-toluic acid) melts at 47° and is unaltered by heating at 150° for half an hour, since the acid solidified again on cooling and melted at the same temperature as before. It is readily soluble in most organic solvents, but rather sparingly so in cold water or light petroleum. When its solution in light petroleum is allowed to evaporate spontaneously, the acid separates in magnificent, glistening prisms. The solution of the sodium salt decolorises permanganate instantly, but the acid is not reduced when it is treated with a large excess of sodium amalgam in the cold. The aqueous solution of the acid gives with ammoniacal cuprous chloride an immediate dense yellow precipitate of the copper derivative. The determination of the dissociation constant of ψ -*m*-toluic acid gave $k = 0\cdot01307$, which is considerably higher than that of *m*-toluic acid ($k = 0\cdot00514$).

Salts of ψ -m-Toluic Acid.—The basicity of the acid was determined by titration with standard caustic potash solution, when 0·1299 neutralised 0·072 KOH, whereas this amount of a monobasic acid, C₈H₈O₂, should neutralise 0·0727 KOH. The neutral solution of the ammonium salt gives no precipitate with barium, calcium, zinc, or magnesium chlorides ; copper sulphate gives no precipitate in the cold, but, on warming, a deep blue copper salt separates.

The *silver* salt, like the corresponding silver salt of $\Delta\gamma$ -butinene- α -carboxylic acid (p. 827), has an abnormal composition. It was prepared by adding excess of silver nitrate to a cold, slightly alkaline solution of the ammonium salt, and obtained in the form of a voluminous, white precipitate, which was collected by the aid of the pump, washed with warm water, alcohol, and ether, and dried over sulphuric acid in a vacuum desiccator. Although only slowly affected by light, this salt is highly explosive, and the silver had therefore to

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be determined as chloride by heating the salt with hydrochloric and nitric acids in a sealed tube. Two different preparations gave the following results:

0.3615 gave 0.3035 AgCl. Ag = 63.1.

0.1704 „ 0.1464 AgCl. Ag = 64.6.

$C_8H_7O_2Ag, AgOH$ requires Ag = 58.7; $C_8H_7O_2Ag, 2AgOH$ requires Ag = 65.7 per cent.

These analyses indicate that the salt, prepared in the above manner, is a mixture of varying quantities of the two silver salts, $C_8H_7O_2Ag, AgOH$ and $C_8H_7O_2Ag, 2AgOH$.

Ethyl ψ -m-toluate, $(CH_3C \cdot CH_2)_2CH \cdot CO_2Et$, was prepared by adding the pure acid (20 grams) to a cold mixture of alcohol (100 c.c.) and sulphuric acid (10 c.c.), and, after remaining for a week, the solution was mixed with water and the ester extracted with ether. The ethereal solution was washed with water and dilute sodium carbonate, the ether evaporated, and the ester distilled under reduced pressure:

0.1250 gave 0.3334 CO_2 and 0.0821 H_2O . C = 72.7; H = 7.3.

$C_{10}H_{12}O_2$ requires C = 73.1; H = 7.3 per cent.

Ethyl ψ -m-toluate is a colourless oil which possesses a pleasant, ethereal odour and distils at 113° (20 mm.). On hydrolysis it yields ψ -m-toluic acid, showing that no molecular change had taken place during its preparation.

The density, magnetic rotation, and refractive power of ethyl ψ -m-toluate and of a very pure specimen of ethyl *m*-toluate were determined by Sir W. H. Perkin with the following results:

Ethyl ψ -m-Toluate.

Density:

$d_{10^\circ/10^\circ} = 1.0052$; $d_{15^\circ/15^\circ} = 1.0009$; $d_{20^\circ/20^\circ} = 0.9971$.

Magnetic rotation:

<i>t.</i>	Sp. rot.	Mol. rot.
15.4°	1.3031	11.876

Refractive power:

$d_{15.3^\circ/4^\circ} = 0.99993$.

μ .	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d} p$.
α1.45795	0.45798	75.109
β1.46806	0.46809	76.767
γ1.47397	0.47401	77.737

Dispersion, $\gamma - \alpha = 2.628$.

Ethyl m-Toluate, b. p. 231° (750 mm.).

Density :

$$d\ 10^{\circ}/10^{\circ} = 1.0374 ; d\ 15^{\circ}/15^{\circ} = 1.0336 ; d\ 20^{\circ}/20^{\circ} = 1.0301.$$

Magnetic rotation :

<i>t.</i>	Sp. rot.	Mol. rot.
15.5°	1.6746	14.773

Refractive power :

$$d\ 14.5^{\circ}/4^{\circ} = 1.03313.$$

	μ .	$\frac{\mu - 1}{d}$	$\frac{\mu - 1}{d}p$.
α	1.50468	0.48850	80.114
β	1.52085	0.50415	82.680
γ	1.53124	0.51420	84.329

Dispersion, $\gamma - \alpha = 4.215$.

These values are interesting in several ways. In the first place they show clearly the close relationship existing between ethyl ψ -*m*-toluate and ethyl $\Delta\gamma$ -butinene- α -carboxylate.

Ethyl $\Delta\gamma$ -butinene- α -carboxylate, $\text{CH}:\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, may be regarded as acetic ester in which hydrogen has been replaced by the group $\text{CH}:\text{C}\cdot\text{CH}_2\cdot$, and the value for this group may therefore be calculated by subtracting the rotation of ethyl acetate (4.462) from that of ethyl $\Delta\gamma$ -butinene- α -carboxylate (8.129) and amounts to 3.667. Since, then, ethyl ψ -*m*-toluate, $(\text{CH}:\text{C}\cdot\text{CH}_2)_2\text{CH}\cdot\text{CO}_2\text{Et}$, is acetic ester in which two atoms of hydrogen have been replaced by two $\text{CH}:\text{C}\cdot\text{CH}_2\cdot$ groups, it is clear that the magnetic rotation of this ester may be calculated in the following way :

	Mol. rot.
Acetic ester	4.462
2 $\text{CH}:\text{C}\cdot\text{CH}_2\cdot$ replacing 2H	7.334
Ethyl ψ - <i>m</i> -toluate (calc.).....	11.796

This number agrees well with that actually found (11.876), and this fact is strong evidence in favour of the views of the constitutions of $\Delta\gamma$ -butinene- α -carboxylic acid and ψ -*m*-toluic acid which have been adopted in these communications. Another point of interest in connexion with the relationship between ψ -*m*-toluic and *m*-toluic acids is the remarkable rise in magnetic rotation and also in refractive power and dispersion which accompanies the intramolecular change from the ψ -acid to the benzene derivative, as is well seen from the following comparison :

	Mol. rot.	Refraction.	Dispersion.
ψ - <i>m</i> -Toluic ester	11.876	75.109	2.628
<i>m</i> -Toluic ester	14.773	80.114	4.215

Mr. E. C. C. Baly kindly undertook to determine the ultra-violet absorption spectra of ψ -*m*-toluic acid and *m*-toluic acid, and the absorption curves of these substances are shown in the accompanying figure.

Mr. Baly adds the following comment. " ψ -*m*-Toluic acid shows a small absorption band which is undoubted evidence of some form of tautomerism, and this may, possibly, be due to the mobility of two hydrogen atoms of the two $\cdot\text{CH}_2\cdot$ groups, and may be expressed thus :

There is a very striking difference between the curves of ψ -*m*-toluic

and *m*-toluic acids, for, although they are of the same shape, the benzenoid absorption occurs at a hundred times the dilution at which the absorption of the ψ -acid occurs. This is clear evidence that ψ -*m*-toluic acid is not benzenoid in character, since simple benzene derivatives do not exhibit their absorption spectra at such great concentrations ($N/10$)."

*Conversion of Δ^5 -Heptadi-inene- δ -carboxylic Acid (ψ -*m*-Toluic Acid) into *m*-Toluic Acid.*

This remarkable intramolecular change takes place readily under the following conditions.

(a) *By Boiling with Water*.—When ψ -*m*-toluic acid is boiled with water for two hours it completely dissolves and, on cooling, a crystalline acid separates which melts at 110—111° and consists of pure *m*-toluic acid.

0.0944 gave 0.244 CO₂ and 0.052 H₂O. $\bar{C}$ = 70.5, $\bar{H}$ = 6.1.

C₈H₈O₂ requires C = 70.5; H = 5.9 per cent.

The same result is obtained when the acid is digested with dilute hydrochloric or sulphuric acids.

(b) *By the Action of Hydrobromic Acid in the Cold*.—In carrying out this experiment, ψ -*m*-toluic acid (1 gram) was dissolved in a cold solution of hydrogen bromide in acetic acid (saturated at 0°, 5 grams), and, after standing overnight, the solution was allowed to evaporate over solid potash in a vacuum desiccator, when an almost colourless, crystalline residue remained which, after crystallisation from light petroleum, melted at 110° and consisted, as direct comparison showed, of pure *m*-toluic acid.

(c) *By the Action of Phosphorus Pentachloride*.—This experiment, made with the object of preparing the amide of ψ -*m*-toluic acid, resulted in the formation of the amide of *m*-toluic acid. ψ -*m*-Toluic acid (6 grams) was mixed with phosphorus pentachloride (10 grams) and, when the reaction had subsided, the liquid was warmed until the pentachloride had completely dissolved. The product was cooled and then added, drop by drop, to concentrated aqueous ammonia surrounded by ice. A good deal of a dark tarry mass separated, this was filtered off, and the filtrate, on standing, deposited crystals of an amide which separated from ether in colourless needles and melted at 93°:

0.1959 gave 16.2 c.c. nitrogen at 12.5 and 758 mm. N = 9.7.

C₈H₉O₂N requires N = 9.3 per cent.

That this substance was the amide of *m*-toluic acid and not of

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ψ -*m*-toluic acid was proved by hydrolysis with alcoholic potash, when it yielded pure *m*-toluic acid of melting point 110°. Moreover, Remsen and Reid (*Amer. Chem. J.*, 1899, 21, 290) state that the amide of *m*-toluic acid melts at 94°.

THE SCHUNCK LABORATORY,
THE VICTORIA UNIVERSITY OF MANCHESTER.