359. *The Structure of the Glutaconic Acids and Esters. Part VI. Derivatives of β-Phenylglutaconic Acid.*

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THE discovery (Kon and Watson, this vol., p. 1) that the two isomeric α-benzyl- or α-ethyl-β-methylglutaconic acids differ not only in configuration but also in the position of the double bond establishes a new principle of some importance. The nature of the substituents should exert a considerable effect on the relative stability of the isomerides and might even determine the occurrence of the other two possible isomerides (*trans*-αβ and *cis*-βγ). There is already some evidence to show that acids with light substituents, such as the αβ-dimethyl acids, tend to exist principally as the *cis*-forms, the *trans* being somewhat unstable.

A phenyl group attached to the β- or central carbon atom of a three-carbon system generally has a stabilising effect on both possible isomerides (compare Johnson and Kon, J., 1926, 2748); the isomeric forms of β-phenyl-α-methylglutaconic acid should therefore be more tractable than the αβ-dimethylglutaconic acids and at the same time provide an example of acids with a bulky substituent in the β-position. No fewer than four isomeric forms have been described. Thorpe and Wood (J., 1913, **103**, 1569) described three of them, termed respectively normal (I), m. p. 120°, *cis*-labile, m. p. 108°, and *trans*-labile, m. p. 155°, the last two being stereoisomerides of the αβ-acid (II). Feist (*Annalen*, 1924, **428**, 25) described a new *cis*-acid, m. p. 151°, and at the same time called in question the existence of the normal and the *cis*-labile acid. He esterified the *trans*-acid, m. p. 155°, and his new *cis*-acid with hot alcoholic sulphuric acid and obtained in both cases mixtures of αβ- and βγ-unsaturated esters. From this he concluded that the esters were desmotropic mixtures, but that the acids were stereoisomerides and both possessed the αβ-structure (II), as neither could be resolved into optically active enantiomerides (the βγ-acid should be resolvable).

$CO_2H{\cdot}CMe{\cdot}CPh[H]{\cdot}CH{\cdot}CO_2H$ (I.)

$CO_2H{\cdot}CMe{:}CPh{\cdot}CH_2{\cdot}CO_2H$ (II.)

Since esterification under Feist's conditions leads to extensive isomerisation, it appeared desirable to repeat Feist's ozonisation experiments and incidentally ascertain the structure of Thorpe and Wood's normal and *cis*-labile acids.

The acids were prepared under both Feist's and Thorpe and Wood's conditions and the *trans*-acid, m. p. 155°, and the *cis*-acid, m. p. 151°, were obtained, but not the two lower-melting acids.

The *cis*-acid readily passes into the anhydride, m. p. 94°, which on careful treatment with tepid water yields an acid, m. p. 146—148°, rising to 151° after one crystallisation from benzene; acids of much lower m. p. are obtained on more drastic treatment. There seems to be little doubt that the acid, m. p. 151°, is the primary product formed on hydration of the anhydride.

The two pure acids were converted through their silver salts into their esters: when these were oxidised with ozone, it was at once apparent that the ester derived from Thorpe and Wood's *trans*-acid, m. p. 155°, had the βγ-structure (III), and the ester of Feist's *cis*-acid was the αβ-isomeride (IV).

$CO_2Et{\cdot}CHMe{\cdot}CPh{:}CH{\cdot}CO_2Et$ (III.)

$CO_2Et{\cdot}CMe{:}CPh{\cdot}CH_2{\cdot}CO_2Et$ (IV.)

The esters so obtained were practically free from their respective isomerides, the latter being detected by qualitative means only.

By methylating ethyl β-phenylglutaconate through its potassio-derivative in a neutral solvent (this is formed, as already found with ethyl β-methylglutaconate, without change of configuration; compare preceding paper), an apparently homogeneous *trans*-βγ-ester was obtained which was very similar in properties to the ester prepared from the acid, m. p. 155°, and gave oxidation products derived solely from the βγ-form (oxalic acid and ethyl benzoylpropionate). The corresponding *cis*-ester could not be prepared in the same way because *cis*-β-phenylglutaconic acid is not known. A small amount of the corresponding acid, however, was isolated, as its sparingly soluble barium salt, in the course of the separation of the other two acids; these had been prepared by a comparatively short hydrolysis of the tricarboxylic ester.

The new *acid*, m. p. 130—131°, appears to be a *cis*-form because it reacts very readily with warm acetyl chloride with the formation of the hydroxy-anhydride, m. p. 94°. It cannot be regenerated from this, the *cis*-acid, m. p. 151°, being formed instead, and therefore cannot be identical with either of Thorpe and Wood's normal and *cis*-labile acids, which are stated to be formed from this anhydride.

Oxidation of the ester of the new acid showed that the double bond was in the βγ-position. The acid is therefore stereoisomeric with the *trans*-acid, m. p. 155°.

The new acid is converted, as already stated, into the same anhydride as the acid, m. p. 151°, but as only the latter is obtained on hydration of the anhydride, it seems reasonable to assume that both the anhydride and Feist's *cis*-acid have the double bond in the same position (αβ). The dehydration of the new acid evidently involves a tautomeric change.

The comparative stability of the new acid affords a good example of the stabilising effect of the β-phenyl group. Apart from this, the phenylmethylglutaconic acids are similar to the acids studied by Kon and Watson in occurring principally in two stable modifications which are both isomeric and stereoisomeric; there is, however, a difference in that the *cis*-form is alkali-stable in the present instance, whilst the *trans*-acid is alkali-stable in the benzylmethyl acids; the stability of the phenylated acids to hydrochloric acid cannot be compared, as they are rapidly decomposed by this reagent.

We have so far failed to convert the *cis*-αβ-acid into its *trans*-form by irradiation with ultra-violet light.

The observations previously made on the tricarboxylic esters from which these esters are ultimately derived (Gidvani, Kon, and Wright, this vol., p. 1027) have been extended. Further evidence has been obtained for the formulation adopted for the yellow sodio-derivative of ethyl carbethoxyphenylglutaconate, to which the structure (V) was tentatively assigned. This compound is changed by mere boiling with alcohol into a colourless isomeride, identical with that obtained by the action of sodium ethoxide on the free ester, evidently possessing the formula (VI), and from which the free ester is regenerated in a few minutes by the action of benzoic acid.

$(CO_2Et)_2CH{\cdot}CPh{:}CNa{\cdot}CO_2Et$ (V.)

$(CO_2Et)_2CNa{\cdot}CPh{:}CH{\cdot}CO_2Et$ (VI.)

Ethyl sodiocyanoacetate condenses with ethyl phenylpropiolate in exactly the same way as ethyl sodiomalonate and gives a brown sodio-derivative, which is not methylated in a neutral solvent and from which the ester is not liberated except by the action of mineral acids or very prolonged treatment with benzoic acid. On boiling with alcohol it passes into a nearly colourless isomeride, which is readily methylated and from which the ester is liberated almost instantly. These compounds can therefore be formulated in the same way as (V) and (VI).

The free ester, ethyl α-cyano-β-phenylglutaconate, decomposes on distillation, but oxidation of the crude ester, liberated from its brown sodio-derivative by means of hydrochloric acid, shows that the ester is an equilibrium mixture of two forms (VII) and (VIII),

$CO_2Et{\cdot}C(CN){:}CPh{\cdot}CH_2{\cdot}CO_2Et$ (VII.)

$CO_2Et{\cdot}CH(CN){\cdot}CPh{:}CH{\cdot}CO_2Et$ (VIII.)

whilst the ester regenerated by means of benzoic acid appears to consist solely of the βγ-ester (VIII).

The methylation of these esters was of great importance, since it has been shown that the coresponding β-methyl ester (ethyl α-cyano-β-methylglutaconate) is methylated abnormally, the methyl group entering the γ-position, in accordance with the constitution of the sodio-compound, which is derived from the αβ-form of the ester (Kon and Nanji, J., 1931, 560).

The methyl derivative is readily obtained either from the original brown sodio-ester of the type (V) in alcoholic solution or from the colourless isomeride, analogous to (VI), in a neutral solvent. The methylated ester (IX) cannot be purified by distillation, but the oxidation products obtained from it show clearly that the methyl group has entered the α-position. The phenylated cyano-esters are thus entirely analogous to the carbethoxy-esters in this respect.

$CO_2Et{\cdot}CMe(CN){\cdot}CPh{:}CH{\cdot}CO_2Et$ (IX.)

$(CO_2Et)_2CMe{\cdot}CPh{:}CH{\cdot}CO_2Et$ (X.)

Ethyl α-carbethoxy-β-phenyl-α-methylglutaconate (X), unlike other similarly constituted esters, does not lose a carbethoxyl group on treatment with sodium ethoxide (Thorpe and Wood, *loc. cit.*). This observation has been confirmed; the ester was recovered unchanged after some days. This exceptional stability is not due to the formation of a sodio-derivative, because all efforts to cause alkylation have been unsuccessful, but it can be readily explained on the basis of the electronic theory.

The elimination of the carbethoxyl (or acetyl) group in compounds of the same general type is evidently caused by the inability of the system to meet the demand for electrons of the two negative groups in the α-position. In a system still retaining an atom of hydrogen this demand would be met by the attraction of the electrons binding this hydrogen, resulting finally in the removal of the hydrogen as a proton and the production of the corresponding enolide ion. In a "blocked" system with a strongly-held alkyl group in place of the potentially ionisable hydrogen, the electron demand of the negative groups can only be met at the expense of the surrounding medium, should a suitable source of electrons (ethoxide ions) be available. One of the negative groups then becomes attached to the latter with the production of a molecule of an ester (ethyl carbonate or acetate). It is the more readily enolisable group which is removed in this way, *e.g.*, acetyl in preference to carbethoxyl and carbethoxyl in preference to cyano (compare the alkylation of ethyl *iso*dehydracetate; Kon and Watson, *loc. cit.*).*

In the present instance it would appear that the electron demand of the carbethoxyl groups can be met by electron displacements involving the phenyl group, which can function both as an electron-accepting and an electron-donating group ($+T$ and $-T$ effect) (compare Ingold, *Ann. Reports*, 1928, **25**, 121); in this case it exercises the latter effect and thus prevents the acquisition of the necessary electron from the ethoxyl ion, which would result in the elimination of the carbethoxyl group.

Owing to the difficulties attending the preparation of β-phenylated glutaconic acid derivatives, an attempt was made to apply the well-known method of Conrad and Guthzeit (*Annalen*, 1883, **222**, 259), benzotrichloride being used in place of chloroform. A poor yield of a colourless sodio-derivative is obtained on condensing this compound with ethyl sodiomalonate, and this gives an undistillable ester on acidification. Oxidation with ozone shows that this ester is not the expected glutaconic acid derivative; the products, ethyl

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* The authors are indebted to Dr. E. M. Watson for drawing their attention to these facts.

mesoxalate and ethyl benzoate, are evidently derived from an ethoxy-ester of the formula $Ph\cdot C(OEt){:}C(CO_2Et)_2$.

EXPERIMENTAL.

β-Phenyl-α-methylglutaconic Acids.—These were prepared essentially as described by Thorpe and Wood (*loc. cit.*) and purified by conversion into the Ba salts, the theo. amount of cold $2N$-NH_3 being used. The *trans*-acid was recovered from the hot filtered solution. The pptd. Ba salts, after extraction with hot H_2O, yielded a mixture of acids on acidification, and these were obtained pure by repeating the above process, the *cis*-acid being obtained by acidifying the insol. Ba salt. The same result is also obtained by Feist's method (*loc. cit.*), in which the mixture of *cis*- and *trans*-tricarboxylic esters is hydrolysed and the acids formed are separated as above. For the final purification of the acids, it is advisable to repeat the pptn. of the Ba salts in the cold.

The pptd. salt is usually completely sol. in much cold H_2O, but in some preps., especially when the hydrolysis of the tricarboxylic ester was only partial, a portion of the salt remained undissolved. From this material the new cis-*acid* (cis-*α-methyl-Δ^β-propene-αγ-dicarboxylic acid*) was obtained on careful acidification; m. p. 130—131° after 3 crystns. from C_6H_6 (Found: C, 65·2; H, 5·4. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%).

When the solid tricarboxylic ester (X) was kept for 5 days with cold 5% KOH aq. and enough EtOH to give a homogeneous solution, a new *acid* was isolated; it crystallised from C_6H_6–petroleum in plates, m. p. 87°, and reduced $KMnO_4$, but was not isomeric with the phenylmethylglutaconic acids; its constitution has not been ascertained (Found: C, 62·2; H, 6·4. $C_8H_{10}O_3$ requires C, 62·3; H, 6·5%).

Ethyl trans-*β-Phenyl-α-methyl-Δ^β-propene-αγ-dicarboxylate* (III).—The *trans*-acid, m. p. 155°, was converted into the ethyl ester by Kon and Watson's method (*loc. cit.*, p. 5), which was employed throughout this work; it had b. p. 165°/5 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0838, $n_D^{20\cdot0^\circ}$ 1·5158, $[R_L]_D$ 76·94.

Ozonisation. This was carried out exactly as described by Kon and Watson (*loc. cit.*, p. 5). The acid products were $H_2C_2O_4$, $Et\cdot CO_2H$, and $Ph\cdot CO_2H$. The neutral products gave the following fractions on distillation under 22 mm.: (i) below 60°, (ii) 60—100°, (iii) 100—160°. Fraction (i) gave no colour with $FeCl_3$ and contained ethyl glyoxylate (phenylhydrazone, m. p. and mixed m. p. 157°). Fraction (ii) also gave no colour with $FeCl_3$ and consisted of ethyl benzoylpropionate, which was identified by means of its *semicarbazone*, m. p. 201° (Found: C, 59·7; H, 6·5. $C_{13}H_{17}O_3N_3$ requires C, 59·3; H, 6·5%). The same semicarbazone was also formed from a specimen of the ester prepared by Hope and Perkin's method (J., 1909, **95**, 2045); the pure ester does not give a colour with $FeCl_3$. Fraction (iii), which was very small, gave a red colour with $FeCl_3$, indicating the presence of ethyl benzoylacetate.

The ester ozonised therefore consisted of the βγ-compound, but contained a very small amount of the αβ-isomeride.

Ethyl β-Phenylglutaconate.—This ester was prepared as described by Ruhemann (J., 1899, **75**, 248) and had b. p. 167—168°/5 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·1014, $n_D^{20\cdot0^\circ}$ 1·5240, $[R_L]_D$ 72·82; it gave ethyl glyoxylate, ethyl benzoylacetate and $H_2C_2O_4$ on ozonisation.

Methylation. The potassio-derivative was prepared with alcohol-free KOEt

(Kon and Nanji, *loc. cit.*) in dry Et_2O and rapidly precipitated in a cryst. condition; the original ester was recovered from it unchanged by treatment with $Ph{\cdot}CO_2H$ in Et_2O. The potassio-derivative, suspended in dry Et_2O, was boiled with an excess of MeI for 1 hr.; the methylated ester isolated from the filtered solution had b. p. 165—166°/6 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0840, $n_D^{20\cdot0^\circ}$ 1·5145, $[R_L]_D$ 76·76, and was evidently the pure *trans-βγ*-ester because it gave the same oxidation products as the ester described above, but none of the fractions gave a colour with $FeCl_3$; $H_2C_2O_4$, ethyl glyoxylate, and ethyl benzoylpropionate were again isolated and identified.

Ethyl cis-*β-Phenyl-α-methyl-Δ^α-propene-αγ-dicarboxylate* (IV).—The ester had b. p. 163°/5 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0982, $n_D^{20\cdot0^\circ}$ 1·5292, $[R_L]_D$ 77·58.

Ozonisation. The ozonide obtained from this ester deposited a solid form, m. p. 150° (compare Feist, *loc. cit.*). The ozonide (both solid and liquid) gave on decomposition a small amount of $H_2C_2O_4$, indicating the presence of *αβ*-ester in the initial material. The following fractions were obtained from the neutral portion of the product at 18 mm.: (i) 70—90°, (ii) 90—145° (iii) 145—160°. The first fraction gave no colour with $FeCl_3$ and contained ethyl pyruvate (semicarbazone, m. p. and mixed m. p. 206°). Fraction (iii) consisted of ethyl benzoylacetate; it gave a deep red colour with $FeCl_3$ and readily formed 1 : 3-diphenylpyrazolone, m. p. and mixed m. p. 136°. The middle fraction was a mixture of the other two.

Ethyl cis-*β-Phenyl-α-methyl-Δ^β-propene-αγ-dicarboxylate.*—The new *cis*-acid, m. p. 131°, gave an ester, b. p. 159°/4 mm., which showed signs of solidifying on keeping; the amount of solid formed was not sufficient to investigate separately.

Ozonisation. The results obtained were similar to those recorded for the *trans*-ester; distinct traces of ethyl benzoylacetate were observed amongst the neutral products; ethyl benzoylpropionate was isolated in the form of its semicarbazone and $H_2C_2O_4$, $Ph{\cdot}CO_2H$ and $Et{\cdot}CO_2H$ were again identified. The ester is therefore the *βγ*-compound, accompanied by a small amount of the *αβ*-isomeride.

Ethyl α-Cyano-β-phenylglutaconate (VII and VIII).—Attempts to obtain this ester by an extension of Rogerson and Thorpe's method (J., 1905, **87**, 1669) were unsuccessful, no condensation taking place between ethyl benzoylacetate and ethyl cyanoacetate in presence of NaOE or KOEt or " molecular " Na; a very poor yield of ester was formed with piperidine and its identity established by hydrolysis to phenyldihydroxypyridine (Ruhemann, J., 1899, **75**, 248).

Ethyl cyanoacetate (28·3 g.) was gradually added to " molecular " Na (5·75 g.), suspended in dry C_6H_6 (250 c.c.); after 2 hrs. ethyl phenylpropiolate (43·5 g.) was added, and the mixture heated under reflux over-night. The solvent was then distilled off, and dry petroleum (b. p. 40—60°) added; the light brown *sodio*-derivative (62 g.) was washed with Et_2O and dried in vac. (Found : Na, 7·4. $C_{16}H_{16}O_4NNa$ requires Na, 7·4%).

The sodio-derivative was covered with H_2O and Et_2O, and a slight excess of cold dil. HCl added with shaking. The ester formed was isolated by evaporation of the dried Et_2O solution; it could not be further purified, as it decomposed on attempted distillation.

Ozonisation. The crude ester was ozonised and the decomposition products were taken up in Et_2O; the Et_2O extract was *not* washed with $NaHCO_3$ aq. On evaporating it and keeping the residue, yellowish crystals of ethyl α-cyanobenzoylacetate, m. p. 40—41°, separated and were collected, the filtrate being again taken up in Et_2O and washed with $NaHCO_3$ aq., which removed a quantity of $H_2C_2O_4$. The neutral products were isolated and distilled, the following fractions being obtained at 12 mm.: (i) below 50°, (ii) 120—135°, (iii) 135—165°, (iv) a little unchanged ester which decomposed on further heating. Fraction (i) consisted of ethyl glyoxylate (phenylhydrazone, m. p. and mixed m. p. 157°). Fraction (ii) gave no colour with $FeCl_3$ and formed the phenylhydrazone of ethyl cyanoglyoxylate, m. p. and mixed m. p. 127° (Kon and Nanji, *loc. cit.*). The highest fraction gave a rich red colour with $FeCl_3$ and contained ethyl benzoylacetate, recognised by the formation of 1 : 3-diphenylpyrazolone, m. p. and mixed m. p. 136°. The ester ozonised was thus a mixture of the $\alpha\beta$- and the $\beta\gamma$-form.

Ethyl α-Cyano-β-phenyl-Δ^β-propene-αγ-dicarboxylate (VIII).—The sodio-derivative (17 g.) was suspended in dry Et_2O (300 c.c.), dry $Ph{\cdot}CO_2H$ (6·3 g.) added, and the mixture mechanically shaken for 3 days. The ester was isolated by evaporation of the Et_2O solution, but could not be distilled.

Ozonisation. This was carried out as described above; only products derived from the $\beta\gamma$-form (VIII) were isolated, namely, ethyl glyoxylate, ethyl α-cyanobenzoylacetate, $H_2C_2O_4$, $Ph{\cdot}CO_2H$, and $CH_2(CO_2H)_2$.

Another specimen of the $\beta\gamma$-ester was prepared by converting the equilibrium ester into the potassio-derivative and treating this with $Ph{\cdot}CO_2H$ (Kon and Nanji, *loc. cit.*); the liberation of the ester was in this instance complete in 2 hrs. The results of ozonisation were the same as those given above.

Hydrolysis. Both acid and alkaline hydrolysis of the cyano-esters gave phenyldihydroxypyridine, m. p. 254—255° (Ruhemann, *loc. cit.*), as sole product.

Ethyl α-Cyano-β-phenyl-α-methyl-Δ^β-propene-αγ-dicarboxylate.—All attempts to convert the original brown sodio-derivative (p. 2449) into the methylated ester in a neutral solvent were fruitless, although the potassium compound prepared from the equilibrium ester was completely methylated by boiling with an excess of MeI in Et_2O or C_6H_6 for 8 hrs. The brown sodio-ester was, however, converted into the same methylated ester by boiling with an excess of MeI in EtOH for 36 hrs. The new ester could not be purified, as it decomposed on attempted distillation.

Ozonisation. The methylated ester was ozonised and the products were worked up as usual. $H_2C_2O_4$, $Ph{\cdot}CO_2H$, and $CHMe(CO_2H)_2$ were isolated and identified, and the neutral products gave the following fractions under 12 mm.: (i) below 40°, (ii) 40—120°, (iii) 120—130°; none of these gave a colour with $FeCl_3$. Fraction (i) consisted of ethyl glyoxylate, which was identified as before. No characteristic solid derivatives could be obtained from the other two fractions, but the absence of the readily identifiable ethyl cyanoglyoxylate and ethyl α-cyanobenzoylacetate, together with the isolation of $CHMe(CO_2H)_2$, indicates that the methylation must have been complete and that the Me group had entered the α-position.

Ethyl Sodio-α-carbethoxy-β-phenylglutaconate (VI).—The yellow sodio-derivative (V) (Michael, *J. pr. Chem.*, 1894, **49**, 20; Gidvani, Kon, and Wright, *loc. cit.*) was boiled with dry EtOH for 4—5 hrs., the solid becoming colourless: it was washed with Et_2O and dried (Found: Na, 6·4. $C_{18}H_{21}O_6Na$ requires Na, 6·5%). The new *sodio*-derivative was treated with $Ph{\cdot}CO_2H$ in Et_2O as described above; the pptn. of $Ph{\cdot}CO_2Na$ began immediately and the regeneration of the ester was complete in 1 hr.; it was isolated by evaporation of the Et_2O solution and consisted entirely of the solid ester, m. p. 38°.

Action of Sodium Ethoxide on Ethyl α-Carbethoxy-β-phenyl-α-methylglutaconate.—The methylated ester (Thorpe and Wood, *loc. cit.*) (35 g.) was dissolved in 40 c.c. of EtOH and added to a solution of 2·3 g. of Na in 30 c.c. of EtOH; the solution assumed a deep orange colour. After 24 hrs. it was acidified with dil. HCl in the presence of Et_2O, and the ester isolated in the usual manner. 25 G. of the original ester were recovered, b. p. 178—180°/5 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·211, $n_D^{20\cdot0^\circ}$ 1·5080, $[R_L]_D$ 92·58; this solidified completely on keeping, m. p. and mixed m. p. 50°. The experiment was repeated with a specimen of the ester prepared by the condensation of ethyl sodiomethylmalonate with ethyl phenylpropiolate (Gidvani, Kon, and Wright, *loc. cit.*), which we succeeded in purifying by distillation; it had b. p. 180—182°/4 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·1207, $n_D^{20\cdot0^\circ}$ 1·5090; it was again recovered unchanged and the same result was obtained when the reaction mixture was kept for 4 days.

Methylation. The ester was added to NaOEt as above, and the mixture treated with an excess of MeI after 12 hrs.; it was then boiled until neutral (12 hrs.). A small amount of ethyl carbonate was recovered and the main fraction of the product had a somewhat lower b. p. and density than the ester from which it was derived, perhaps owing to the admixture of some dicarboxylic ester, but it was impossible to separate this by fractionation; the *cis*-*αβ*-acid, m. p. 151°, was obtained from it on hydrolysis, but no trace of a dimethyl acid appeared to be formed.

Condensation of Ethyl Sodiomalonate with Benzotrichloride.—Ethyl sodiomalonate, prepared with the aid of "molecular" Na in C_6H_6, could not be condensed with benzotrichloride, the initial materials being recovered unchanged.

Ethyl malonate (80 g.) was added to a solution of 23 g. of Na in 450 c.c. of EtOH, and 50 g. of $Ph\cdot CCl_3$ were gradually introduced into the warm solution with vigorous shaking; a further 15 g. were finally added and the mixture was heated on the steam-bath for 30 mins. The dark brown solution was filtered hot, and the pptd. salt washed with hot EtOH until colourless. The filtrate and washings deposited a solid on cooling; this was collected, dissolved in H_2O, and acidified with dil. HCl, and the liberated ester isolated with Et_2O. It gave a dirty violet colour with $FeCl_3$ and could not be distilled even under 2 mm. pressure.

Ozonisation. The neutral portion of the ozonisation product gave the following fractions under 12 mm.: (i) 60—80°, (ii) 80—120°, neither giving a colour with $FeCl_3$. The lower fraction was greenish-yellow and gave the hydrate of ethyl mesoxalate, m. p. and mixed m. p. 59°, on treatment with H_2O. The higher fraction had the characteristic smell of $Ph\cdot CO_2Et$ and gave $Ph\cdot CO_2H$ on hydrolysis; a small amount of $H_2C_2O_4$, probably formed from ethyl mesoxalate, was also isolated.

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