

796. *Unsaturated Systems. Part IV.* The ortho-Claisen Rearrangement of α - and γ -Aryloxy- β -methylcrotonates and α -Phenoxy- γ -methylcrotonate.*

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Methyl α - and γ -bromo- β -methylcrotonate have been converted into the phenoxy, *p*-tolylxy-, and 2,6-dimethylphenoxy-derivatives. The *ortho*-Claisen rearrangement of methyl β -methyl- α - and γ -phenoxy- and -*p*-tolylxy-crotonate and of methyl γ -methyl- α -phenoxycrotonate is described.

α -Aryloxycrotonates.—It has been established that in the reaction of α -bromo- β -methylcrotonic acid with alkoxides,¹ sodium hydroxide, and piperidine² a prototropic shift to give 2-bromo-3-methylbut-3-enoic acid precedes replacement of bromine, and the nature of the product is determined by the reaction conditions. With alkoxides and piperidine the product of S_N2 reaction only was isolated, and with sodium hydroxide both S_N2 and S_N1 products were isolated. The bromo-acid did not react appreciably with refluxing methanolic sodium phenoxide in 24 hours, whereas 50% of reaction was observed with 0.8N-sodium phenoxide in refluxing dioxan in the same period. However, methyl α -bromo- β -methylcrotonate (I), on account of its greater mobility due to the presence of the ester group, reacted readily with sodium phenoxide in benzene (55% yield) or with phenol and potassium carbonate in acetone (84% yield). The reaction is presumably of the S_N2 type with the $\beta\gamma$ -form (II) of the ester, but the only product isolated was methyl β -methyl- α -phenoxycrotonate (IVa). The $\alpha\beta$ -unsaturated ester results because the position of equilibrium would be on the $\alpha\beta$ -side owing to the presence of the α -phenoxy-group ($-I$, $+T$). The structure of methyl β -methyl- α -phenoxycrotonate (IVa) was established by hydrolysis to the acid whose structure was established by (a) hydrogenation to the known β -methyl- α -phenoxybutyric acid³ and (b) ozonolysis to give acetone (2,4-dinitrophenylhydrazone); absence of isomerisation during this hydrolysis follows from the fact that the

* Part III, *J.*, 1960, 1262.

¹ Owen, *J.*, 1949, 236.

² Owen and Sultanbawa, *J.*, 1949, 3089.

³ Bischoff, *Ber.*, 1900, **33**, 937.

EXPERIMENTAL

Light absorption was determined for ethanol solutions with a Unicam S.P. 500 spectrophotometer.

Attempted Reaction of α -Bromo- β -methylcrotonic Acid with Sodium Phenoxide.—No appreciable reaction was observed on refluxing the acid with phenol and (a) methanolic 1.7N-sodium hydroxide for 24 hr. or (b) aqueous N-sodium hydroxide for 12 hr. However, refluxing the acid with 0.8N-sodium phenoxide in dioxan for 24 hr. caused 50% of the bromine to be replaced (Volhard estimation).

Methyl β -Methyl- α -phenoxycrotonate.—(a) *Reaction in benzene.* Phenol (2.35 g.) and sodium (0.58 g.) in benzene (40 ml.) were refluxed until all the sodium had reacted. Methyl α -bromo- β -methylcrotonate (4.83 g.) in benzene (10 ml.) was added all at once and the mixture refluxed at 150° for 12 hr. The product was worked up by ether-extraction, etc. *Methyl β -methyl- α -phenoxycrotonate* (2.92 g., 55%) had b. p. 90—91°/3 mm., n_D^{29} 1.5165, and λ_{\max} 219 m μ (ϵ 14,360) (Found: C, 69.7; H, 6.7. $C_{12}H_{14}O_3$ requires: C, 69.9; H, 6.85%). (b) *Reaction in acetone.* Phenol (18.0 g.), potassium carbonate (17.9 g.), and methyl α -bromo- β -methylcrotonate (2.50 g.) in acetone (250 ml.) were refluxed for 12 hr. The acetone was removed under reduced pressure, and the residue dissolved in water and worked up as before. *Methyl β -methyl- α -phenoxycrotonate* (22.5 g., 84%) had b. p. 86—90°/1 mm. and n_D^{31} 1.5185.

β -Methyl- α -phenoxycrotonic Acid.—Methyl β -methyl- α -phenoxycrotonate (15.0 g.) was heated for 10 min. with boiling 7 : 3 aqueous-methanolic N-sodium hydroxide (150 ml.), and the acid was isolated in the usual manner. *β -Methyl- α -phenoxycrotonic acid* (14.0 g.) formed needles [from light petroleum (b. p. 60—80°)], m. p. 118°, λ_{\max} 219 m μ (ϵ 15,820) (Found: C, 68.6; H, 6.15. $C_{11}H_{12}O_3$ requires C, 68.7; H, 6.3%).

This acid (0.50 g.) in methanol (25 ml.) was hydrogenated at atmospheric pressure over palladised charcoal. The product, β -methyl- α -phenoxybutyric acid, crystallised from methanol, had m. p. 82° (lit.,³ 81.5—82.3°).

The crotonic acid (0.50 g.) in glacial acetic acid (50 ml.), on ozonisation and steam-distillation, gave acetone, which was isolated as the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 126°.

Methyl α -Phenoxycrotonate.—(a) *Reaction in benzene.* Phenol (2.35 g.) and sodium (0.50 g.) benzene (25 ml.) were refluxed until the sodium had reacted. Methyl α -bromocrotonate (4.48 g.) in benzene (15 ml.) was added, and the mixture was refluxed for 12 hr., left at 29° for 10 hr., and worked up as above. *Methyl α -phenoxycrotonate* (3.44 g., 72%) had b. p. 92—94°/2 mm., n_D^{27} 1.5200 (Found: C, 68.9; H, 6.2. $C_{11}H_{12}O_3$ requires C, 68.75; H, 6.3%). (b) *Reaction in acetone.* Phenol (2.35 g.), potassium carbonate (3.85 g.), and methyl α -bromocrotonate (4.50 g.) in acetone (40 ml.) were refluxed for 12 hr. Working up gave methyl α -phenoxycrotonate (3.40 g., 71%), b. p. 94°/2 mm., n_D^{31} 1.5190.

Methyl α -phenoxycrotonate (1.00 g.) was heated at 95° for 5 min. with 7 : 3 aqueous-methanolic N-sodium hydroxide and worked up in the usual manner. *α -Phenoxycrotonic acid* (0.85 g.) was obtained as needles (from water), m. p. 119° (Found: C, 67.6; H, 5.7. $C_{10}H_{10}O_3$ requires C, 67.4; H, 5.65%).

The acid (0.50 g.) in methanol (25 ml.) was hydrogenated at atmospheric pressure over palladised charcoal. The resulting α -phenoxybutyric acid formed needles [from light petroleum (b. p. 60—80°)], m. p. 82° (lit.,³ 82—83°).

Methyl α -phenoxycrotonate (0.50 g.) in carbon tetrachloride (25 ml.) was ozonised for 45 min. Carbon tetrachloride was distilled under reduced pressure, and the product was steam-distilled with zinc and acetic acid. Acetaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 147°, was isolated from the distillate.

Methyl β -Methyl- α -p-tolylloxycrotonate.—*p*-Cresol (13.40 g., excess), potassium carbonate (10.8 g.), and methyl α -bromo- β -methylcrotonate (15 g.) in acetone (200 ml.) were refluxed for 12 hr. and the product was worked up in the usual way, affording *methyl β -methyl- α -p-tolylloxycrotonate* (12.75 g., 75%), b. p. 108—110°/0.5 mm., n_D^{31} 1.5155, λ_{\max} 224 m μ (ϵ 15,480) (Found: C, 70.8; H, 7.3. $C_{13}H_{16}O_3$ requires C, 70.9; H, 7.3%).

Hydrolysis as above gave *β -methyl- α -p-tolylloxycrotonic acid* (7.10 g.), needles (from methanol), m. p. 104°, λ_{\max} 224 m μ (ϵ 16,010) (Found: C, 69.7; H, 6.7. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.85%).

Methyl α -Bromo- γ -methylcrotonate.— α -Bromo- γ -methylcrotonic acid (the authors thank

Mr. B. J. P. Alles for providing the acid) was esterified with diazomethane at 0°. The methyl ester (22.20 g.) had b. p. 76—80°/10 mm., n_D^{29} 1.4778.

Methyl γ -Methyl- α -phenoxycrotonate.—Phenol (15.0 g.), potassium carbonate (15.66 g.), and methyl α -bromo- γ -methylcrotonate (21.80 g.) in acetone (250 ml.) were refluxed for 12 hr. and set aside overnight. Working up gave *methyl γ -methyl- α -phenoxycrotonate* (18.0 g., 77%), b. p. 102—103°/0.5 mm., n_D^{29} 1.5115, λ_{\max} 216, 272 m μ (ϵ 13,550, 1640) (Found: C, 70.05; H, 6.75. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.85%).

Hydrolysis of the ester (15.85 g.) as above gave a liquid (probably $\beta\gamma$ -unsaturated) acid (2.10 g.) and *γ -methyl- α -phenoxycrotonic acid* (11.40 g.), needles (from aqueous alcohol), m. p. 112°, λ_{\max} 210, 213 m μ (ϵ 17,020, 16,560) (Found: C, 68.85; H, 6.25. $C_{11}H_{12}O_3$ requires C, 68.75; H, 6.3%).

Reaction of Methyl α -Bromo- β -methylcrotonate with 2,6-Dimethylphenol.—2,6-Dimethylphenol (28.0 g.), potassium carbonate (21.07 g.), and methyl α -bromo- β -methylcrotonate (29.45 g.) in acetone (300 ml.) were refluxed for 24 hr. and the product was worked up in the usual way. Methyl α -bromo- β -methylcrotonate (6.70 g.) was recovered unchanged. The product (20.30 g., 74%) was separated into a low-boiling and a high-boiling fraction. The former (10.80 g., 39%) was *methyl 2-(2,6-dimethylphenoxy)-3-methylbut-3-enoate*, b. p. 101—103°/10⁻³ mm., n_D^{30} 1.5040, λ_{\max} 205 m μ (ϵ 15,670) (Found: C, 71.8; H, 7.7. $C_{14}H_{18}O_3$ requires C, 71.75; H, 7.75%). The high-boiling fraction (9.50 g., 34%) was *methyl α -(2,6-dimethylphenoxy)- β -methylcrotonate*, b. p. 132—133°/10⁻³ mm., n_D^{30} 1.5270, λ_{\max} 278—280 m μ (ϵ 1500) (ϵ 40,250 at 205 m μ) (Found: C, 71.4; H, 7.6. $C_{14}H_{18}O_3$ requires C, 71.75; H, 7.75%).

The low boiling ester (7.00 g.) was hydrolysed as above, giving the corresponding *acid* (86%) that formed needles [from light petroleum (b. p. 60—80°)], m. p. 83°, λ_{\max} 205 m μ (ϵ 14,860) (Found: C, 70.8; H, 7.3. $C_{13}H_{16}O_3$ requires C, 70.85; H, 7.3%).

α -(2,6-Dimethylphenoxy)- β -methylcrotonic Acid.—The above $\alpha\beta$ -unsaturated ester (7.50 g.) was hydrolysed 30% methanolic N·NaOH (75 ml.) and the acid was isolated in the usual as above, giving *α -(2,6-dimethylphenoxy)- β -methylcrotonic acid*, needles [from benzene—light petroleum (b. p. 60—80°)], m. p. 115°, λ_{\max} 256, 280 m μ (ϵ 1590, 2490) (ϵ 34,600 at 205 m μ) (Found: C, 70.75; H, 7.25. $C_{13}H_{16}O_3$ requires C, 70.85; H, 7.3%).

Action of Sodium Hydroxide on the above $\alpha\beta$ - and $\beta\gamma$ -Unsaturated Acids.—(a) The $\beta\gamma$ -unsaturated acid (0.50 g.), m. p. 83°, was refluxed with 10% aqueous sodium hydroxide (20 ml.) for 12 hr., and then cooled, acidified, and extracted with ether. The dried (Na_2SO_4) extracts gave an acid which, crystallised from benzene—light petroleum (b. p. 60—80°), had m. p. 115°, undepressed on admixture with the $\alpha\beta$ -unsaturated acid. (b) The $\alpha\beta$ -unsaturated acid (0.50 g.), m. p. 115°, was refluxed with 10% sodium hydroxide (20 ml.) for 12 hr. and worked up as in (a). The unchanged $\alpha\beta$ -unsaturated acid, m. p. and mixed m. p. 115°, was obtained.

Reactions of Methyl γ -Bromo- β -methylcrotonate with Phenol.—Phenol (4.7 g., 0.05 mole), benzene (25 ml.), and sodium wire (1.2 g., 0.05 g.-atom) were refluxed till all the sodium had dissolved. Methyl γ -bromo- β -methylcrotonate (9.65 g., 0.05 mole) was added at once to the cooled solution. The mixture was refluxed for 12 hr. at 135—140°, then cooled, poured into water, and extracted with ether. The ether—benzene extract was washed with N-sodium hydroxide, dried (Na_2SO_4), and evaporated. Methyl β -methyl- γ -phenoxycrotonate (6.5 g., 93%) had b. p. 116—118°/3 mm., n_D^{32} 1.5210 (lit.,⁵ b. p. 118—120°/2 mm., n_D^{22} 1.5258) (Found: C, 69.6; H, 6.85. Calc. for $C_{12}H_{14}O_3$: C, 69.9; H, 6.8%).

The above reaction was carried out under a variety of conditions (see Table). The product was mainly methyl β -methyl- γ -phenoxycrotonate or a mixture of this ($\alpha\beta$ -unsaturated ester) and methyl 4-phenoxy-3-methylbut-3-enoate. The mixture could not be separated by distillation. Preparation of compounds described below was carried out under conditions that gave mainly the $\alpha\beta$ -unsaturated ester.

β -Methyl- γ -phenoxycrotonic Acid.—Methyl β -methyl- γ -phenoxycrotonate (1.00 g.) was subjected to short hydrolysis according to the earlier procedure.¹⁵ β -Methyl- γ -phenoxycrotonic acid (0.90 g.) was obtained as needles [from light petroleum (b. p. 60—80°)], m. p. 76° (lit.,⁵ 108—109°) (Found: C, 68.8; H, 6.25. Calc. for $C_{11}H_{12}O_3$: C, 68.75; H, 6.25%).

The following γ -aryloxycrotonates and their acids were prepared according to the procedure just given: Methyl γ -phenoxycrotonate, b. p. 83—85°/1.3 \times 10⁻² mm., n_D^{29} 1.5245 (Found: C, 68.85; H, 6.3. Calc. for $C_{11}H_{12}O_3$: C, 68.75; H, 6.25%). γ -Phenoxycrotonic

Solvent	Reagent	Period (hr.)	Temp.	Yield (%)
Benzene	NaOPh (from Na-PhOH)	5	130°	49.5
"	"	12	135—140°	93
Toluene	"	5	150—160	75
Dioxan	"	5	"	66
Toluene	NaOPh (from NaH-PhOH)	5	"	56
Acetone *	PhOH-K ₂ CO ₃	6	100	75
"	"	12	"	94
"	"	24	"	78
Ether *	NaOPh (from NaOMe-PhOH)	192	35	54
"	"	240	"	58

* Acetone or ether was evaporated before the mixture was poured into water.

acid, m. p. 135° (lit.,^{5,16} 136°) (Found: C, 67.5; H, 5.4. Calc. for C₁₀H₁₀O₃: C, 67.4; H, 5.65%) *Methyl β-methyl-γ-p-tolyloxycrotonate* (75%), b. p. 102—104°/1.84 × 10⁻² mm., n_D²⁰ 1.5185 (Found: C, 70.75; H, 7.25. C₁₃H₁₆O₃ requires C, 70.9; H, 7.3%), and the corresponding acid, needles (from aqueous alcohol), m. p. 101—102° (Found C, 69.9; H, 6.8. C₁₂H₁₄O₃ requires C, 69.9; H, 6.85%). *Methyl γ-(2,6-dimethylphenoxy)-β-methylcrotonate* (87%), b. p. 113—114°/10⁻² mm., n_D²⁰ 1.5160 (Found: C, 71.8; H, 7.8. C₁₄H₁₈O₃ requires C, 71.75; H, 7.75%). *γ-(2,6-Dimethylphenoxy)-β-methylcrotonic acid* (from aqueous methanol), m. p. 85° (Found: C, 70.7; H, 7.3. C₁₃H₁₆O₃ requires C, 70.85; H, 7.3%).

Rearrangement of Methyl β-Methyl-γ-phenoxycrotonate.—(a) *Methyl β-methyl-γ-phenoxycrotonate* (4.00 g.) was refluxed at 270—280° for 3 hr. The product was cooled and the unchanged ester (1.00 g.) was filtered off. The solid product (2.50 g., 74%) was purified by steam-distillation and yielded pale yellow plates [from light petroleum (b. p. 60—80°)] of 3-isopropylidenebenzofuran-2(3H)-one, m. p. 97°, λ_{max}, 246, 282 mμ (ε 12,540, 8180) (Found: C, 75.95; H, 5.75. Calc. for C₁₁H₁₀O₃: C, 75.85; H, 5.8%).

(b) The ester (3.00 g.) and diethylaniline (3.00 g.) were refluxed at 240—250° for 3 hr. The product, after removal of the diethylaniline with dilute hydrochloric acid, was taken up in light petroleum (b. p. 60—80°) and washed with 10% sodium hydroxide solution. Evaporation of the dried (Na₂SO₄) petroleum extract gave a mixture (2.34 g.) of the benzofuranone and the starting ester. The sodium hydroxide extract was acidified and extracted with ether, and the extracts were dried (Na₂SO₄) and evaporated. The benzofuranone (0.16 g.), m. p. 97°, was obtained.

Attempted Rearrangement of Methyl 3-Methyl-4-phenoxybut-3-enoate.—The ester (3.00 g.) was refluxed at 300° for 6 hr. The unchanged ester, b. p. 158°/2 mm., n_D³⁰ 1.5190, was recovered.

3-Isopropylidenebenzofuran-2(3H)-one.—(a) *Action of sodium hydroxide.*—The benzofuranone (0.32 g.) was refluxed with 7:3 aqueous-methanolic N-sodium hydroxide (30 ml.) for ½ hr. The solution was cooled, extracted with ether, acidified, and extracted with ether. The latter ether extracts were dried (Na₂SO₄) and afforded the benzofuranone, m. p. 97°.

(b) *Ozonisation.* The benzofuranone (0.40 g.) in carbon tetrachloride was ozonised for 45 min. and the carbon tetrachloride was removed under reduced pressure. The residue was treated with zinc dust, water, and acetic acid and steam-distilled. The distillate afforded acetone 2,4-dinitrophenylhydrazone (0.20 g.), m. p. and mixed m. p. 126°.

(c) *Ozonisation and oxidation.* The benzofuranone (0.5 g.) was ozonised in carbon tetrachloride (30 ml.) for an hour at 0°. Carbon tetrachloride was removed under reduced pressure and the residue was refluxed with water (10 ml.) for 2 hr. The mixture was cooled and extracted with ether, and the extract washed with sodium carbonate solution. On acidification of the sodium carbonate extract, a solid acid (0.15 g.) separated that crystallised from water and was shown to be salicylic acid, m. p. and mixed m. p. 158°.

Rearrangement of β-Methyl-γ-phenoxycrotonic Acid.—This acid (3.0 g.) was refluxed at 300° for 3 hr. and the product was distilled, giving fractions (1), b. p. 46—66°/0.31 mm. (1.18 g.), n_D³¹ 1.5265—1.5160, (2) b. p. 70—118°/0.31 mm. (0.32 g.), n_D³¹ 1.4965, and (3) b. p. 118°/0.31 mm. (0.72 g.), m. p. 97°. The first two fractions were phenolic and gave a violet colour with ferric chloride. The last fraction was 3-isopropylidenebenzofuran-2(3H)-one (0.72 g., 26.5%). Fraction 1, on redistillation, gave 3-methyl-4-phenoxybut-3-enoic acid, b. p. 77—78°/0.5 mm., n_D³¹ 1.5095 (Found: C, 68.75; H, 6.45. C₁₁H₁₂O₃ requires C, 68.75; H, 6.3%). Schotten-Baumann treatment of this acid gave phenyl benzoate, m. p. and mixed m. p. 71°.

¹⁶ Canonica, Fiechi, and Valcavi, *Atti accad. naz. Lincei. Rend. Classe Sci. fis. mat. nat.*, 1957, **18**, 520.

*Rearrangement of Methyl β -Methyl- γ -*p*-tolylloxycrotonate.*—This ester (3.00 g.) was refluxed at 300° for 3 hr., then cooled, and filtered. Steam-distillation gave 3-isopropylidene-5-methylbenzofuran-2(3H)-one (2.0 g., 70%) as greenish-yellow crystals [from light petroleum (b. p. 60—80°)], m. p. 134°, λ_{\max} , 246, 282 μ (ϵ 13,880, 8250) (Found: C, 76.25; H, 6.5. $C_{12}H_{12}O_2$ requires C, 76.55; H, 6.4%).

3-Isopropylidene-5-methylbenzofuran-2(3H)-one.—(a) *Ozonolysis.* The benzofuranone (0.30 g.) in carbon tetrachloride was ozonised at 29° for an hour and the product was worked up as above, to give acetone 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 126°.

(b) *Ozonolysis and oxidation.* The benzofuranone (0.97 g.) was ozonised in carbon tetrachloride (35 ml.) for 2 hr. Working up the product as above gave 2-hydroxy-5-methylbenzoic acid m. p. and mixed m. p. 152° (lit.,¹⁷ m. p. 151°).

*Rearrangement of β -Methyl- γ -*p*-tolylloxycrotonic Acid.*—(a) The acid (1.80 g.) was refluxed at 310° for 3 hr. and the product distilled, giving the fractions, (1) b. p. 60—110°/0.5 mm. (0.45 g.), n_D^{30} 1.5140—1.5120, (2) b. p. 110—122°/0.5 mm. (0.35 g.), n_D^{30} 1.5215, and (3) b. p. 122°/0.5 mm. (0.05 g.), m. p. 134°. The first two fractions were phenolic and gave a violet colour with ferric chloride. By the Schotten-Baumann procedure they gave *p*-tolyl benzoate, m. p. and mixed m. p. 72° (due to the presence of 4-*p*-tolyloxy-3-methylbut-3-enoic acid). The last fraction gave the benzofuranone, m. p. 134°.

(b) The crotonic acid (3.0 g.) was heated at 270° for 2 hr., then cooled, and the benzofuranone (1.00 g., 39%) was filtered off. It formed greenish-yellow crystals, m. p. 134°, from light petroleum (b. p. 60—80°).

Attempted Rearrangement of Methyl γ -Phenoxycrotonate.—Methyl γ -phenoxycrotonate (0.50 g.) was refluxed at 260—280° for 4 hr. and the product distilled. Unchanged ester (0.28 g.) distilled at 80—82°/0.01 mm., having n_D^{31} 1.5190. Heating the ester in diethylaniline for 1½ hr. or in a sealed tube for 3 hr. was without effect. The ester charred when heated in a sealed tube at 320° for 12 hr.

Attempted Rearrangement of γ -Phenoxycrotonic Acid.— γ -Phenoxycrotonic acid (1.0 g.) was refluxed at 300° for 3 hr. A tarry undistillable product was obtained.

Rearrangement of β -Methyl- α -phenoxycrotonic Acid.—Sodium (1.25 g.) was dissolved in diethylene glycol (15 ml.), and β -methyl- α -phenoxycrotonic acid (3.00 g.) was added. The mixture was refluxed at 270° for 12 hr., cooled, diluted with water, acidified, and extracted with ether. The extract was washed with sodium carbonate solution, and the alkaline extract was acidified and extracted with ether. The dried (Na_2SO_4) ether extract, on evaporation, gave 4-*o*-hydroxyphenyl-3-methylbut-3-enoic acid (1.95 g., 65%), b. p. 138—142°/0.5 mm., n_D^{31} 1.5225, λ_{\max} , 244, 280 μ (ϵ 3200, 2240) (Found: C, 68.25; H, 6.85. $C_{11}H_{12}O_3$ requires C, 68.75; H, 6.3%).

The rearranged acid (0.50 g.) in ethanol (30 ml.) was hydrogenated over palladised charcoal at atmospheric pressure. Partial hydrogenation took place over 18 hr. ($1H_2 = 64.5$ ml.; only 30 ml. were absorbed, probably owing to original partial formation of lactone instead of acid). The mixture was filtered, ethanol evaporated, and the residue dissolved in ether. Evaporation of the dried (Na_2SO_4) ether solution gave an oil which was dissolved in light petroleum (b. p. 60—80°) and set aside for a week. A solid and a liquid acid separated. The solid was γ -*o*-hydroxyphenyl- β -methylbutyric acid, m. p. 110° (Found: C, 68.0; H, 7.3. $C_{11}H_{14}O_3$ requires C, 68.05; H, 7.3%).

*Ozonolysis of 4-*o*-Hydroxyphenyl-3-methylbut-3-enoic Acid.*—This acid (0.50 g.) in carbon tetrachloride was cooled in a freezing mixture and ozonised for 1 hr. The carbon tetrachloride was removed under reduced pressure and the residue treated with zinc dust and acetic acid and steam-distilled. The 2,4-dinitrophenylhydrazone obtained from the distillate was chromatographed on alumina with chloroform. Only salicylaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 248°, was obtained. Ozonolysis in acetic acid at 0° or in carbon tetrachloride at 29° gave the same result.

*Rearrangement of β -Methyl- α -phenoxycrotonic Acid and Conversion into Methyl 4-*o*-Hydroxyphenyl-3-methylbut-3-enoate.*—To a solution of sodium (3.07 g.) in diethylene glycol (25 g.) was added β -methyl- α -phenoxycrotonic acid (8.0 g.), and the mixture was refluxed for 12 hr. then cooled, diluted with water, acidified, and extracted with ether. The extract was washed with sodium carbonate solution and water, dried (Na_2SO_4), and evaporated, giving an oil

¹⁷ Ja, Ber., 1878, 11, 375.

(0.8 g.) which was not investigated. The sodium carbonate extract was acidified and extracted with ether. This extract was dried (Na_2SO_4), treated at 0° with an excess of ethereal diazomethane, and kept at 0° for 5 hr. The ether was removed and the residue dissolved again in ether, washed with sodium carbonate solution and water, and dried (Na_2SO_4). Evaporation then gave *methyl 4-o-hydroxyphenyl-3-methylbut-3-enoate* (6.60 g., 82.5%), b. p. $123\text{--}125^\circ/9.35 \times 10^{-2}$ mm., n_D^{30} 1.5365, λ_{max} 210, 245, 286 μ (ϵ 18,300, 7320, 2810) (Found: C, 70.2; H, 7.0. $\text{C}_{12}\text{H}_{14}\text{O}_3$ requires C, 69.9; H, 6.85%), giving a green colour with ferric chloride.

This ester (1.00 g.) was hydrogenated over palladised charcoal at atmospheric pressure for 8 hr. The product (0.75 g.), b. p. $118\text{--}123^\circ/0.15$ mm., n_D^{30} 1.5120, gave a green colour with ferric chloride. It was hydrolysed as above to the butyric acid, needles (from water), m. p. and mixed m. p. 110° .

The rearranged ester (0.30 g.) was ozonised as above; it gave only salicylaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 248° .

Methyl 4-o-Methoxyphenyl-3-methylbut-3-enoate.—A solution of 4-o-hydroxyphenyl-3-methylbut-3-enoic acid (3.0 g.) in *n*-sodium hydroxide (50 ml.) was shaken with dimethyl sulphate (4 ml., excess) at 0° , then made alkaline with sodium hydroxide and heated at 95° for 90 min. The mixture was again cooled, acidified, and extracted with ether. To the dried (Na_2SO_4) extract at 0° was added ethereal diazomethane. Treatment as above gave *methyl 4-o-methoxyphenyl-3-methylbut-3-enoate* (2.44 g., 71%), b. p. $140\text{--}142^\circ/2$ mm., n_D^{30} 1.5315, λ_{max} 209, 245, 286 μ (ϵ 19,580, 8570, 3970) (Found: C, 70.7; H, 7.3. $\text{C}_{13}\text{H}_{16}\text{O}_3$ requires C, 70.85; H, 7.3%).

The ester (0.25 g.) was ozonised in carbon tetrachloride for 1 hr. at 0° ; it gave only *o*-methoxybenzaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 250° .

Rearrangement of β -Methyl- α -p-tolyloxycrotonic Acid.—To a solution of sodium (2.03 g.) in diethylene glycol (20 g.) was added β -methyl- α -p-tolyloxycrotonic acid (5.00 g.), and the mixture was refluxed at 260° , then cooled, diluted with water, acidified, and extracted with ether. The extract was washed with sodium carbonate solution and water and dried (Na_2SO_4); evaporation gave an oil (0.5 g.) which was not investigated. The sodium carbonate extract was acidified and extracted with ether. This extract dried (Na_2SO_4) and evaporated, giving a semi-solid (3.70 g., 74%). This was treated in ether with ethereal diazomethane at 0° as above, yielding *methyl 4-(2-hydroxy-5-methylphenyl)-3-methylbut-3-enoate*, b. p. $123\text{--}125^\circ/10^{-2}$ mm., n_D^{30} 1.5250, λ_{max} 292 μ (ϵ 2830) (Found: C, 71.15; H, 7.2. $\text{C}_{13}\text{H}_{16}\text{O}_3$ requires C, 70.85; H, 7.3%).

This product (0.50 g.) was hydrogenated at atmospheric pressure over palladised charcoal for 18 hr. The hydrogenated ester was hydrolysed as above, giving γ -(2-hydroxy-5-methylphenyl)- β -methylbutyric acid, needles (from water), m. p. $110\text{--}111^\circ$ (Found: C, 68.9; H, 7.85. $\text{C}_{12}\text{H}_{16}\text{O}_3$ requires C, 69.2; H, 7.75%).

The preceding butenoate (0.37 g.) was ozonised in carbon tetrachloride at 0° for 90 min.; it gave only 2-hydroxy-5-methylbenzaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 258° (Found: C, 53.3; H, 4.15; N, 17.3. $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_5$ requires C, 53.15; H, 3.85; N, 17.7%). The authentic derivative was prepared from the known aldehyde.¹⁸

Rearrangement of γ -Methyl- α -phenoxycrotonic Acid.—To a solution of sodium (2.13 g.) in diethylene glycol (20 g.) was added γ -methyl- α -phenoxycrotonic acid (5.00 g.), and the mixture was refluxed for 12 hr. The rearranged acid was worked up as before and esterified with ethereal diazomethane at 0° , giving *methyl 4-o-hydroxyphenylpent-3-enoate* (3.18 g., 64%), b. p. $112\text{--}114^\circ/10^{-2}$ mm., n_D^{30} 1.5310, λ_{max} 270, 279 μ (ϵ 1920, 2760) (Found: C, 70.0; H, 7.0. $\text{C}_{12}\text{H}_{14}\text{O}_3$ requires C, 69.9; H, 6.85%).

This ester (0.50 g.) in ethanol (30 ml.) was hydrogenated at atmospheric pressure over palladised charcoal. Partial hydrogenation took place in 24 hr. Hydrolysis of the product gave a mixture of the acid of the starting ester and the hydrogenated acid, m. p. 90° .

The ester (0.50 g.) in 10% aqueous sodium hydroxide (30 ml.) was heated at 95° and Raney nickel alloy (3 g.) was added in small portions with stirring. The mixture was stirred for 1 hr. at 95° , then cooled, acidified, and extracted with ether. Evaporation of the dried (Na_2SO_4) ether extract gave γ -*o*-hydroxyphenylvaleric acid, m. p. 90° (Found: C, 68.6; H, 7.35. $\text{C}_{11}\text{H}_{14}\text{O}_3$ requires C, 68.05; H, 7.3%).

The rearranged unsaturated ester (0.20 g.) was ozonised in carbon tetrachloride for 45 min.; 2-hydroxyacetophenone 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 210° (lit.,¹⁹ m. p. $211\text{--}212^\circ$), was isolated as above.

¹⁸ Tiemann and Schotten, *Ber.*, 1878, **11**, 767.

¹⁹ McEntree and Pinder, *J.*, 1957, 4419.

Attempted Rearrangement of α -Phenoxycrotonic Acid.—To a solution of sodium (0.98 g.) in diethylene glycol (10 g.) was added α -phenoxycrotonic acid (2.0 g.) and the mixture was refluxed at 260° for 12 hr. Working up gave an undistillable semi-solid material (1.58 g.).

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