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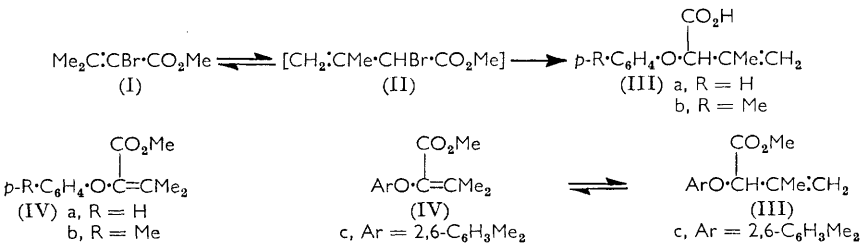
Methyl α- and γ-bromo-β-methylcrotonate have been converted into the phenoxy, *p*-tolyloxy-, and 2,6-dimethylphenoxy-derivatives. The *ortho*-Claisen rearrangement of methyl β-methyl-α- and γ-phenoxy- and -*p*-tolyloxycrotonate and of methyl γ-methyl-α-phenoxycrotonate is described.

α-*Aryloxycrotonates*.—It has been established that in the reaction of α-bromo-β-methylcrotonic acid with alkoxides,[1] sodium hydroxide, and piperidine [2] 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 βγ-form (II) of the ester, but the only product isolated was methyl β-methyl-α-phenoxycrotonate (IVa). The αβ-unsaturated ester results because the position of equilibrium would be on the αβ-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 acid [3] 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.

ester and the acid had the same ultraviolet absorption maximum (219 mμ). By a similar procedure the corresponding α-bromo-esters gave methyl β-methyl-α-*p*-tolyloxycrotonate (IVb), α-phenoxycrotonate, and γ-methyl-α-phenoxycrotonate, and their structures were similarly established. However, in the reaction of methyl α-bromo-β-methylcrotonate with 2,6-dimethylphenol, the 2,6-dimethylphenoxy-ester was obtained in 74% yield but was a mixture of βγ- (39%) (IIIc) and αβ-unsaturated ester (35%) (IVc). These esters were hydrolysed to the acids; the βγ-unsaturated acid, on prolonged treatment with 10% aqueous sodium hydroxide, gave the αβ-unsaturated acid, whereas the αβ-unsaturated acid was unchanged by such treatment; this provided direct evidence for the postulated mechanism in the reaction with phenols. In this particular case, the conversion of the βγ- into the αβ-unsaturated ester is slow owing to the bulky 2,6-dimethylphenoxy-group attached to the carbon atom from which a proton has to be removed.



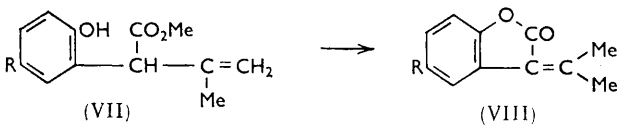

*γ-Aryloxycrotonates.*—Allyl halides react with phenols in acetone in the presence of potassium carbonate or with sodium phenoxide in an inert solvent, *e.g.*, benzene, dioxan, etc., to give the corresponding aryl ethers.[4] In certain cases the reaction in benzene or dioxan gives also the *C*-allylated product. As γ-bromo-αβ-unsaturated esters are readily available by Ziegler bromination of αβ-unsaturated esters, it was of interest to see if the γ-bromo-esters could also give *C*-allylated products. Therefore, methyl γ-bromo-β-methylcrotonate was treated with phenol under a variety of conditions in solvents such as benzene,[5] toluene, dioxan, acetone, and ether;[6] the product was the ether, methyl β-methyl-γ-phenoxycrotonate (though in some experiments mixed with the βγ-unsaturated isomer). The reaction is presumably of the $S_N2$ type. Similarly methyl γ-phenoxycrotonate, methyl β-methyl-γ-*p*-tolyloxycrotonate, and methyl γ-2,6-dimethylphenoxy-β-methylcrotonate were prepared in acetone (they were characterised as the solid γ-aryloxycrotonic acids).

ortho-*Claisen Rearrangement.*—The *ortho*-Claisen rearrangement has been investigated by a large number of workers and recently interest has been focussed on the electronic[7] and steric factors[8] involved. White *et al.*[9] have studied the effect of substituents in the nucleus and have attempted to relate their results to Hammett parameters. However, variations in the substituents on the allyl group have been of limited value. We therefore attempted to rearrange systems which contained an α- or γ-carboxyl group in the allyl chain. As the γ-derivatives were readily available as described above, methyl β-methyl-γ-phenoxycrotonate (VIa) was rearranged at 270—280° (3 hr.). The product (VIIa) eliminated methanol, to give 3-isopropylidenebenzofuran-2(3*H*)-one (VIIIa) in 74% yield. The structure of the benzofuranone was established by ozonolysis which gave acetone (2,4-dinitrophenylhydrazone) and, after oxidation, salicyclic acid (attempts to hydrogenate

[4] Tarbell, in *Org. Reactions*, 1944, Vol. II, p. 1.
[5] Canonica, Fiecchi, and Adobbati, *Rend. Ist. Lombardo Sci., Pt. I, Classe sci. mat. nat.*, 1954, **87**, 257.
[6] Kornblum and Lurie, *J. Amer. Chem. Soc.*, 1959, **81**, 2705.
[7] Marcinkiewicz, Green, and Mamalis, *Tetrahedron*, 1961, **14**, 208.
[8] Marvel, Dupzyk, Stephenson, and Anderson, *J. Org. Chem.*, 1960, **25**, 676.
[9] White, Slater, and Fife, *J. Org. Chem.*, 1961, **26**, 627; White, Gwynn, Schlitt, Girard, and Fife, *J. Amer. Chem. Soc.*, 1958, **80**, 3277; White and Norcross, *ibid.*, 1961, **83**, 3265; White and Fife, *ibid.*, p. 3846.

the benzofuranone cleaved the molecule).[10] These results confirmed the observations of Canonica and Fiecchi.[11] Similarly methyl β-methyl-γ-*p*-tolyloxycrotonate (VIb) was rearranged thermally to 5-methyl-3-isopropylidene-5-methylbenzofuran-2(3*H*)-one (VIIIb) (70% yield) that on ozonolysis gave acetone and, after further oxidation, 2-hydroxy-5-methylbenzoic acid. However thermal rearrangement of β-methyl-γ-phenoxycrotonic acid (cf. VIa) gave 3-isopropylidenebenzofuran-2(3*H*)-one (VIIIa) (27%) together with the double-bond migration product (IXa and its lactone) in 50% yield. The lactone was characterised by analysis and by the fact that on benzoylation it gave phenyl benzoate. Similarly β-methyl-γ-*p*-tolyloxycrotonic acid (cf. VIb) on rearrangement gave the benzofuranone (VIIIb) (39%) together with the βγ-form of the acid (IXb) and its lactone. On the other hand, methyl γ-phenoxycrotonate failed to rearrange, and γ-phenoxycrotonic acid gave a tar.

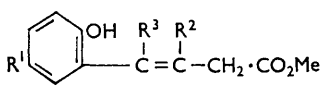
$$Br\cdot CH_2\cdot CMe{=}CH\cdot CO_2Me \longrightarrow R\cdot C_6H_4\cdot O\cdot CH_2\cdot CMe{:}CH\cdot CO_2Me \qquad R\cdot C_6H_4\cdot O\cdot CH{:}CMe\cdot CH_2\cdot CO_2Me$$
(V) (VI) (IX)



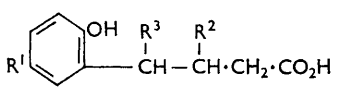
(VII) (VIII)

(Series a, R = H; Series b, R = *p*-Me)

Systems containing an α-carboxyl group in the allyl chain cannot be readily prepared, but it was considered that β-methy-α-phenoxycrotonic acid (cf. IVa) would partly isomerise under alkaline conditions and any βγ-unsaturated acid formed should rearrange in the alkaline medium.[12] Therefore, the sodium salt of the acid was refluxed with an excess of a solution of sodium in diethylene glycol for 12 hours: 4-*o*-hydroxyphenyl-3-methylbut-3-enoic acid was obtained in 65% yield, being characterised as its methyl ester (Xa) and as the methyl ester methyl ether. The structures of this acid and its ester were established by hydrogenation and then characterisation of the product (XIa) and by ozonisation to give salicylaldehyde. Similarly β-methyl α-*p*-tolyloxycrotonic acid (cf. IVb) was rearranged and methyl 4-(2-hydroxy-5-methylphenyl) 3-methylbut-3-enoate (Xb) was obtained, the structure of this being established by hydrogenation to the acid (XIb) and by ozonisation to give 2-hydroxy-5-methylbenzaldehyde as only product. Likewise, γ-methyl-α-phenoxycrotonic acid rearranged smoothly and the product was characterised as methyl 4-(*o*-hydroxyphenyl)pent-3-enoate (Xc), that on hydrogenation, etc., gave γ-*o*-hydroxyphenylvaleric acid (XIc) and on ozonisation gave only *o*-hydroxyacetophenone. Attempts to rearrange α-phenoxycrotonic acid gave an undistillable product.



(X)



(XI)

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a: | H | Me | H |
| b: | Me | Me | H |
| c: | H | H | Me |

The above procedure provides a convenient method for the introduction of a four-carbon chain at the *ortho*-position of phenols, in contrast to the Friedel–Crafts reaction with succinic anhydrides which gives the *para*-substituted product.[13]

The difference in the behaviour of β- and γ-methylcrotonic acid derivatives from that of derivatives of crotonic acid itself confirms the influence of β- and γ-methyl groups in these systems.[14]

[10] See Elderfield, "Heterocyclic Compounds," Wiley, New York, 1950, Vol. I, p. 185.
[11] Canonica and Fiecchi, *Atti accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1954, **17**, 385.
[12] Padmanathan and Sultanbawa, *Proc. Ceylon Assoc. Adv. Sci.*, 1959, **15**, 1; Sultanbawa, *ibid.*, **16**, 123.
[13] Berliner, in *Org. Reactions*, 1949, Vol. V, p. 229.
[14] Sultanbawa, Veeravagu, and Padmanathan, *J.*, 1960, 1262.

## 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 $\lambda_{max.}$ 219 mμ (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°, $\lambda_{max.}$ 219 mμ (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-tolyloxycrotonate.*—*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-tolyloxycrotonate* (12·75 g., 75%), b. p. 108—110°/0·5 mm., $n_D^{31}$ 1·5155, $\lambda_{max.}$ 224 mμ (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-tolyloxycrotonic acid* (7·10 g.), needles (from methanol), m. p. 104°, $\lambda_{max.}$ 224 mμ (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, $\lambda_{max.}$ 216, 272 mμ (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 βγ-unsaturated) acid (2·10 g.) and *γ-methyl-α-phenoxycrotonic acid* (11·40 g.), needles (from aqueous alcohol), m. p. 112°, $\lambda_{max.}$ 210, 213 mμ (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, $\lambda_{max.}$ 205 mμ (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, $\lambda_{max.}$ 278—280 mμ (ε 1500) (ε 40,250 at 205 mμ) (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°, $\lambda_{max.}$ 205 mμ (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 αβ-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°, $\lambda_{max.}$ 256, 280 mμ (ε 1590, 2490) (ε 34,600 at 205 mμ) (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 αβ- and βγ-Unsaturated Acids.*—(*a*) The βγ-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 αβ-unsaturated acid. (*b*) The αβ-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 αβ-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 (αβ-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 αβ-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 × $10^{-2}$ 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

[15] Owen and Sultanbawa, *J.*, 1949, 3098.

| 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–$K_2CO_3$ | 6 | 100 | 75 |
| ,, ..... | ,, | 12 | ,, | 94 |
| ,, ..... | ,, | 24 | ,, | 78 |
| Ether * ..... | NaOPh (fromNaOMe–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 $C_{10}H_{10}O_3$: C, 67·4; H, 5·65%) *Methyl* β-*methyl*-γ-p-*tolyloxycrotonate* (75%), b. p. 102—104°/1·84 × $10^{-2}$ mm., $n_D^{29}$ 1·5185 (Found: C, 70·75; H, 7·25. $C_{13}H_{16}O_3$ 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. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·85%). *Methyl* γ-(2,6-*dimethylphenoxy*)-β-*methylcrotonate* (87%), b. p. 113—114°/$10^{-2}$ mm., $n_D^{29}$ 1·5160 (Found: C, 71·8; H, 7·8. $C_{14}H_{18}O_3$ 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. $C_{13}H_{16}O_3$ 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(3*H*)-one, m. p. 97°, $\lambda_{max.}$ 246, 282 mμ (ε 12,540, 8180) (Found: C, 75·95; H, 5·75. Calc. for $C_{11}H_{10}O_3$: 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 ($Na_2SO_4$) 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 ($Na_2SO_4$) 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., $n_D^{30}$ 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 ($Na_2SO_4$) 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 salicyclic 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.), $n_D^{31}$ 1·5265—1·5160, (2) b. p. 70—118°/0·31 mm. (0·32 g.), $n_D^{31}$ 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(3*H*)-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., $n_D^{31}$ 1·5095 (Found: C, 68·75; H, 6·45. $C_{11}H_{12}O_3$ 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, Fiecchi, and Valcavi, *Atti accad. naz. Lincei. Rend. Classe Sci. fis. mat. nat.*, 1957, **18**, 520.

*Rearrangement of Methyl* β-*Methyl-γ-p-tolyloxycrotonate.*—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°, $\lambda_{max.}$ 246, 282 mμ (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-hydoxy-5-methylbenzoic acid m. p. and mixed m. p. 152° (lit.,[17] m. p. 151°).

*Rearrangement of* β-*Methyl-γ-*p-*tolyloxycrotonic 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, $\lambda_{max.}$ 244, 280 mμ (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—125°/9·35 × $10^{-2}$ mm., $n_D^{30}$ 1·5365, $\lambda_{max.}$ 210, 245, 286 mμ (ε 18,300, 7320, 2810) (Found: C, 70·2; H, 7·0. $C_{12}H_{14}O_3$ 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—123°/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—142°/2 mm., $n_D^{30}$ 1·5315, $\lambda_{max.}$ 209, 245, 286 mμ (ε 19,580, 8570, 3970) (Found: C, 70·7; H, 7·3. $C_{13}H_{16}O_3$ 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—125°/$10^{-2}$ mm., $n_D^{30}$ 1·5250, $\lambda_{max.}$ 292 mμ (ε 2830) (Found: C, 71·15; H, 7·2. $C_{13}H_{16}O_3$ 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—111° (Found: C, 68·9; H, 7·85. $C_{12}H_{16}O_3$ 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. $C_{14}H_{12}N_4O_5$ 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-phenoxycrotinic 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—114°/$10^{-2}$ mm., $n_D^{30}$ 1·5310, $\lambda_{max.}$ 270, 279 mμ (ε 1920, 2760) (Found: C, 70·0; H, 7·0. $C_{12}H_{14}O_3$ 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. $C_{11}H_{14}O_3$ 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—212°), 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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