255. *Unsaturated Systems. Part III.* Synthesis of Some Substituted γ-Methoxycrotonic Acids and Esters.*

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Six substituted γ-bromocrotonic esters afford γ-methoxycrotonates when refluxed for several days with methanolic calcium carbonate. The effects of substituents on the reaction of the crotonic esters with *N*-bromosuccinimide are observed.

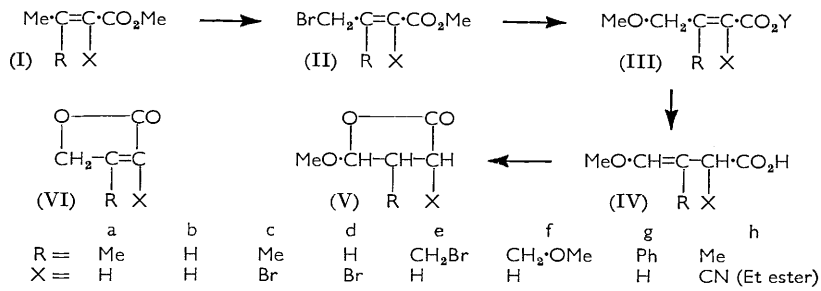
γ-METHOXYCROTONIC ACID (IIIb; Y = H) was first synthesised by the reaction of γ-bromocrotonic acid with sodium methoxide, and in six steps from epichlorohydrin, but attempts to prepare γ-methoxy-β-methyl- and γ-methoxy-β-methoxymethyl-crotonic acid (IIIa and f; Y = H) from the corresponding methoxyacetones by the Reformatsky procedure failed.[1] The solvolysis of γ-bromocrotonates has now been developed as a general method for the preparation of these acids.

Reaction of methyl γ-bromo-β-methylcrotonate with methanolic calcium carbonate in a sealed tube at 100° was 98% complete in about 5 days: it gave a 72% yield of methyl γ-methoxy-β-methylcrotonate after 7 days' refluxing. The ester was hydrolysed to the methoxy-acid with N-alkali at 94—95° in 3 minutes, the solid acid being accompanied by a liquid isomer. The structure of the solid acid was established as (IIIa; Y = H) by hydrogenation to γ-methoxy-β-methylbutyric acid, ozonisation to methoxyacetone, and

* Part II, *J.*, 1958, 4113.

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

isomerisation to the but-3-enoic acid (IVa) by alkali and characterisation of the β-formylbutyric acid. The liquid acid was the but-3-enoic acid (IVa), containing a small amount of the lactone (Va): it gave an immediate precipitate of the 2,4-dinitrophenylhydrazone of β-formylbutyric acid and on hydrogenation in sodium carbonate solution over palladium–charcoal gave γ-methoxy-β-methylbutyric acid.



The acid (IIIa; Y = H) was also obtained by hydrolysing βγ-dibromo-β-methylbutyronitrile with 95% sulphuric acid at room temperature for 7 days and treating the resulting dibromo-acid–amide mixture with sodium methoxide. A solution of the product in concentrated sulphuric acid was then treated with aqueous sodium nitrite; the acid (IIIa; Y = H) was obtained in poor yield.

Attempts were then made to prepare α-bromo-γ-methoxy-β-methylcrotonic acid (IIIc; Y = H) by adding bromine to the acid (IIIa; Y = H) and dehydrobrominating the product.[2] αβ-Dibromo-γ-methoxy-β-methylbutyric acid was obtained as an oil (not characterised) but attempts to dehydrobrominate it gave a mixture of the debrominated acid, dehydrobrominated acid, and bromo-olefin; the bromo-olefin and part of the γ-methoxy-acid (IIIa; Y = H) could be separated, but the required (IIIc; Y = H) could not be obtained pure. On account of this difficulty the solvolysis of γ-bromocrotonates was investigated as a general method for the synthesis of γ-methoxycrotonates.

Methyl γ-bromocrotonate (IIb) was refluxed with an excess of calcium carbonate in methanol, and methyl γ-methoxycrotonate (IIIb; Y = Me) was obtained in 67% yield. It was hydrolysed to the acid (IIIb; Y = H), showing that reaction had again taken place without anionotropic change. Likewise methyl γ-bromo-β-bromomethylcrotonate (IIe) was prepared from methyl β-methylcrotonate (Ia) by reaction with two equivalents of bromosuccinimide in 65% yield and converted into methyl γ-methoxy-β-methoxymethylcrotonate (IIIf; Y = Me) in 67% yield in a similar manner. The ester was hydrolysed in 3 minutes at 95° with N-alkali to the acid which was characterised as its 4-phenylphenacyl ester.

Similarly methyl α-bromo-β-methylcrotonate (Ic) gave methyl αγ-dibromo-β-methylcrotonate (IIc) and α-bromo-γ-methoxy-β-methylcrotonate (IIIc; Y = Me) in good yield. The structure of the last product was confirmed by ozonolysis to methoxyacetone and oxalic acid. In the residues from the distillation both of the bromo-esters (IIc) and (IIIc; Y = Me), a solid (m. p. 64—65°) was isolated which on the basis of its analysis, infrared absorption band at 1739 cm.$^{-1}$, and mode of formation is formulated as α-bromo-γ-hydroxy-β-methylcrotonic acid lactone (VIc).

Attempts were made to see whether methyl αγ-dibromo-β-methylcrotonate (IIc) could be lactonised by heating it in solvents as forerunner of a general method for synthesis of αβ-unsaturated lactones,[3] but the highest yield (obtained in concentrated hydrochloric acid) was 20% (here reaction probably took place through the αγ-dibromo-acid [4]), although

[2] Cf. Owen and Sultanbawa, *J.* 1949, 3105.
[3] Ruzicka, Plattner, and Pataki, *Helv. Chim. Acta*, 1945, **28**, 1360.
[4] Rubin, Paist, and Elderfield, *J. Org. Chem.*, 1941, **6**, 260.

under the same conditions methyl γ-bromo-β-phenylcrotonate (IIg) was converted into β-phenylbutenolide (VIg) in 91% yield. The opportunity was taken to convert methyl γ-bromo-β-phenylcrotonate (IIg) into γ-methoxy-β-phenylcrotonic acid (IIIg; Y = H) which was isolated as a solid along with a liquid acid which is probably a mixture of the αβ- and the βγ-unsaturated acid.

Methyl α-bromocrotonate [5] (Id) and ethyl α-cyano-β-methylcrotonate [6] (Ih) were both brominated in good yield with bromosuccinimide to give methyl αγ-dibromocrotonate (IId) and ethyl γ-bromo-α-cyano-β-methylcrotonate (IIh) respectively, but only the former ester could be converted into the methoxy-compound. There was no evidence for lactone formation in this reaction although reaction with bromosuccimide required 22 hours.

It is not possible to compare the behaviour of αβ-unsaturated ketones,[7] nitriles,[8] and esters [9] towards bromosuccimide owing to the paucity of information, but it had been observed by Ziegler *et al.*[9] that the time taken to brominate methyl crotonate in carbon tetrachloride was 13 hours whereas methyl β-methylcrotonate required only ½ hour. For the latter the time was increased to about 3 hours when ten times the amount of carbon tetrachloride was used.

In the present investigation it has been observed that reaction of bromosuccinimide with methyl crotonate and α-substituted (*e.g.*, Br, OMe [10]) or β-substituted (*e.g.*, Ph, CO_2ET[12]) methyl crotonates in carbon tetrachloride requires about 20 hours whereas with methyl β-methylcrotonate and α-substituted (*e.g.*, Br, OMe,[11] CN) methyl β-methylcrotonates it is complete in less than 2 hours. The evidence for β-methoxy- and β-ethoxy-crotonic esters is conflicting.[13] α- and γ-Methyl [14,15] groups also increase the reactivity of methyl crotonate. Therefore the main consideration for increased reactivity of the methyl crotonates seems to be the presence of an electron-repelling group at the α-, β-, or γ-position.

Experimental

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

Methyl β-methylcrotonate with bromosuccimide gave methyl γ-bromo-β-methylcrotonate,[9] b. p. 74—78°/6 mm., n_D^{28} 1·4990, $\lambda_{max.}$ 221 mμ (ε 11,500).

Reaction of Methyl γ-Bromo-β-methylcrotonate with Calcium Carbonate in Methanol.—The bromo-ester (5·0 g.) was dissolved in methanol and the solution made up to 50 c.c. Portions (5 c.c.) of this solution were heated in sealed Pyrex tubes containing methanol (2 c.c.) and calcium carbonate (0·5 g.) in a boiling-water bath. At intervals the contents of a tube were poured into water and extracted with ether, and the bromide ion in the aqueous solution was determined by Volhard's method. The results were:

Time (hr.)	0	6	11·5	17·5	23	49	70	98·5	122·5	150
Reaction (%)	0·2	24·4	35·5	46·5	53·2	75·1	84·7	94·4	97·7	97·7

Methyl γ-Methoxy-β-methylcrotonate.—Methyl γ-bromo-β-methylcrotonate (96 g.) was refluxed with calcium carbonate (50 g., 100% excess) in anhydrous methanol (200 c.c.) for 7

[5] von Auwers and Harres, *Z. phys. Chem.*, 1929, *A*, **143**, 1.
[6] Cope, Hofmann, Wyckoff, and Hardenberg, *J. Amer. Chem. Soc.*, 1941, **63**, 3452.
[7] Buu-Hoï. *Experientia*, 1946, **8**, 310; Southwick, Pursglove, and Numerof, *J. Amer. Chem. Soc.*, 1950, **72**, 1600; Wassermann, Aubrey, and Zimmermann, *ibid.*, 1953, **75**, 96.
[8] Couvrer and Bruylants, *Bull. Soc. chim. belges*, 1952, **61**, 253; Bailey and Bello, *J. Org. Chem.*, 1955, **20**, 525.
[9] Corey, *J. Amer. Chem. Soc.*, 1953, **75**, 2251; Ziegler, Spath, Schaaf, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 80.
[10] Sultanbawa, *Proc. Ceylon Assoc. Adv. Sci.*, 1953, **9**, Part I, 33.
[11] *Idem, ibid.*, 1952, **8**, Part I, 36; and unpublished results.
[12] Campbell and Hunt, *J.*, 1947, 1176.
[13] Kögl and Bruin, *Rec. Trav. chim.*, 1950, **69**, 729; Reid and Ruby, *J. Amer. Chem. Soc.*, 1951, **73**, 1054.
[14] Inhoffen, Bork, and Schwieter, *Annalen*, 1953, **580**, 1; Inhoffen, Isler, von der Bey, Raspé, Zeller, and Ahrens, *ibid.*, p. 7.
[15] Schmidt and Karrer, *Helv. Chim. Acta*, 1946, **29**, 573; Buchta and Berger, *Annalen*, 1952, **576**, 155.

days. The unchanged calcium carbonate was filtered off and washed with methanol, and most of the methanol was removed under reduced pressure through a Dufton column. The residue was poured into water and extracted with ether, and the ether extracts were dried (Na_2SO_4) and evaporated. The residue on fractionation gave *methyl γ-methoxy-β-methylcrotonate* (51·5 g., 72%), b. p. 64—65°/1 mm., n_D^{29} 1·4440 (Found: C, 58·5; H, 8·5. $C_7H_{12}O_3$ requires C, 58·3; H, 8·4%), $\lambda_{max.}$ 214 mμ (ε 12,000).

γ-Methoxy-β-methylcrotonic Acid.—Methyl γ-methoxy-β-methylcrotonate (20 g.) was added all at once to stirred aqueous N-sodium hydroxide (250 c.c.) at 94—95°. The mixture became homogeneous in 1 min. and after 3 minutes' stirring it was rapidly cooled, acidified (Congo Red) with 4N-sulphuric acid, saturated with sodium chloride, and extracted with ether. The ether extract was dried (Na_2SO_4) and evaporated to give a semi-solid residue (17 g., 85%). By filtration a solid (10 g.) and a viscous pale yellow oil (6·5 g.) were obtained. The solid crystallised from water in colourless needles of *γ-methoxy-β-methylcrotonic acid*, m. p. 84° (Found: C, 55·4; H, 7·8%; equiv., 131. $C_6H_{10}O_3$ requires C, 55·4; H, 7·75%; equiv., 130), $\lambda_{max.}$ 213 mμ (ε 11,100). The *4-phenylphenacyl ester* crystallised from aqueous alcohol in flakes, m. p. 109—110° (Found: C, 73·8; H, 6·2. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

The liquid portion was acidic and had an equivalent weight of 130·8. It was lactonic and unlike the solid acid gave an immediate precipitate with a solution of 2,4-dinitrophenylhydrazine sulphate in 4N-sulphuric acid. This indicated the presence of the βγ-form of the acid. No crystalline 4-phenylphenacyl ester could be obtained from it.

Hydrogenation of γ-Methoxy-β-methylcrotonic Acid.—The methoxy-acid (1·3 g.) was dissolved in a solution of sodium carbonate (0·6 g.) in water (10 c.c.) and hydrogenated over palladium–charcoal (30 mg. on 0·2 g.) at atmospheric pressure. The resulting γ-methoxy-β-methylbutyric acid (1·08 g.) had b. p. 125—126°/20 mm., n_D^{30} 1·4215 (lit.,[16] b. p. 123—125°/20 mm., n_D^{20} 1·4235). It was characterised as its *4-phenylphenacyl ester*, m. p. 55—57° (Found: C, 73·95; H, 7·2. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·8%).

Hydrogenation of the Liquid Acid.—The liquid acid (1·3 g.), when hydrogenated as above, gave γ-methoxy-β-methylbutyric acid, b. p. 125—126°/20 mm., n_D^{28} 1·4225 (4-phenylphenacyl ester, m. p. and mixed m. p. 55—57°).

Base-catalysed Isomerisation of γ-Methoxy-β-methylcrotonic Acid.—The acid (0·25 g.) was heated in 4N-sodium hydroxide (10 c.c.) and on a water-bath for 10 hr., then cooled, acidified (Congo Red) with 4N-sulphuric acid and treated with 1% 2,4-dinitrophenylhydrazine sulphate in 4N-sulphuric acid (500 c.c.). After 2 hr. the precipitate was collected and crystallised from benzene, giving yellow needles of β-formylbutyric acid 2,4-dinitrophenylhydrazone, m. p. 180° (lit.,[1] m. p. 174—175°,[17] 136—138°) (Found: C, 45·0; H, 4·05; N, 18·7. Calc. for $C_{11}H_{12}O_6N_4$: C, 44·6; H, 4·1; N, 18·9%).

Ozonisation of γ-Methoxy-β-methylcrotonic Acid.—The acid (0·6 g.) was ozonised in carbon tetrachloride (10 c.c.) at 0°, the issuing gases being passed through a solution of dimedone reagent. No formaldehyde was formed (dimedone). The oily ozonide, obtained after the removal of carbon tetrachloride, was treated with zinc dust (1·3 g.) and acetic acid (5 c.c.) and steam-distilled. The distillate gave methoxyacetone 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 164—165° (from methanol).

Hydrolysis of βγ-Dibromo-β-methylbutyronitrile and Conversion into γ-Methoxy-β-methylcrotonic Acid.—1-Methylallyl cyanide [18] was converted into βγ-dibromo-α-methylbutyronitrile, b. p. 72°/0·2 mm., n_D^{29} 1·5275, by addition of bromine.[19]

The dibromo-nitrile (20 g.) was dissolved in 95% sulphuric acid (40 g.) and kept at *ca.* 30° for 7 days. Hydrogen bromide was liberated. The acid solution was poured on ice, and the aqueous solution extracted with ether. The ether extract was washed, dried (Na_2SO_4), and evaporated. The liquid residue (14 g.) was dissolved in dry methanol (35 c.c.), kept cooled in a freezing mixture, and treated dropwise a solution from sodium (3·6 g.) in methanol (80 c.c.). The mixture was stirred for 1 hr., then refluxed for ½ hr., cooled, and made acid (Congo Red), and most of the solvent was removed under reduced pressure. The residue was dissolved in water and extracted with ether, and the extract was dried (Na_2SO_4) and evaporated. The residue (3·9 g.) was treated in concentrated sulphuric acid (25 c.c.) at 0° with sodium nitrite

[16] Wagner, *J. Amer. Chem. Soc.*, 1949, **71**, 3214.
[17] Pino and Piacenti, *Rend. Ist. lombardo sci., Pt. I, Classe sci. mat. e nat.*, 1954, **87**, 200.
[18] Tamele, Ott, Marple, and Hearne, *Ind. Eng. Chem.*, 1941, **33**, 115.
[19] Reynold, Fuson, Philip, and Southwick, *J. Amer. Chem. Soc.*, 1944, **66**, 670.

(2 g.) in water (5 c.c.). The mixture was then warmed on a water-bath for 10 min., cooled, and extracted with ether. On removal of the ether from the dried (Na_2SO_4) extract, a semi-solid product (0·8 g.) was obtained. The solid was separated, crystallised from light petroleum (b. p. 40—60°), and shown to be γ-methoxy-β-methylcrotonic acid as its m. p. 83—84° was undepressed by an authentic sample.

Addition of Bromine to γ-Methoxy-β-methylcrotonic Acid.—Bromine (5·5 c.c.) in carbon tetrachloride (50 c.c.) was added during 30 min. to a stirred solution of the acid (13 g.) in carbon tetrachloride (50 c.c.) at 0°. After 3 hr. at 0° the solution became decolorised. On removal of the solvent the dibromo-acid was obtained as a light brown solid (27·8 g., 96%). Attempts to purify it failed.

Attempts to Dehydrobrominate the Above Dibromo-acid.—Several attempts to dehydrobrominate [20] the acid failed. *E.g.*, the dibromo-acid (2·7 g.) in ethanol (10 c.c.) was treated at 0° with ethanolic sodium ethoxide [Na (0·46 g.) in ethanol (10 c.c.)] during 15 min. After reaction at 15—25° ethanol was removed under reduced pressure, the residue dissolved in water, and the neutral fraction extracted with ether. The aqueous solution was acidified (Congo Red) and extracted with ether. The dried ether extracts, on evaporation, gave (*a*) a neutral (0·33 g.) and (*b*) an acid fraction (0·47 g.). Fraction (*a*) on distillation, gave 1-bromo-3-methoxy-2-methylprop-1-ene, b. p. 125—126°/760 mm., n_D^{30} 1·4510. Fraction (*b*) was distilled from a retort under a high vacuum: γ-methoxy-β-methylcrotonic acid, m. p. and mixed m. p. 84°, crystallised on the sides; a clear viscous liquid was obtained as a main fraction (Found: equiv., 166·3; Br, 23·1%. Calc. for γ-methoxy-β-methylcrotonic acid: equiv., 130. Calc. for α-bromo-γ-methoxy-β-methylcrotonic acid: equiv., 209; Br, 38·3%).

Methyl γ-Bromo-β-bromomethylcrotonate.—Methyl β-methylcrotonate (11·4 g.) reacted with bromosuccinimide (38 g.) in carbon tetrachloride (80 c.c.) containing benzoyl peroxide (0·1 g.) in 2 hr. on a water-bath. The solution was cooled, filtered, and evaporated under reduced pressure. Fractionation gave *methyl γ-bromo-β-bromomethylcrotonate* (18 g., 65%), b. p. 70—73°/8·2 × 10^{-3} mm., n_D^{27} 1·5460 (Found: C, 27·0; H, 3·1; Br, 58·7. $C_6H_8O_2Br_2$ requires C, 26·5; H, 3·0; Br, 58·75%).

Methyl γ-Methoxy-β-methoxymethylcrotonate.—Methyl γ-bromo-β-bromomethylcrotonate (17 g.) was refluxed on a water-bath with calcium carbonate (12·5 g.) in anhydrous methanol (50 c.c.) for 14 days and the product was worked up as usual, giving *methyl γ-methoxy-β-methoxymethylcrotonate* (6·8 g., 67%), b. p. 90°/7 mm., $n_D^{28·5}$ 1·4520 (Found: C, 54·9; H, 8·1. $C_8H_{14}O_4$ requires C, 55·2; H, 8·1%), $\lambda_{max.}$ 212 mμ (ε 9700).

γ-Methoxy-β-methoxymethylcrotonic Acid.—To aqueous N-sodium hydroxide (70 c.c.) at *ca.* 95° methyl γ-methoxy-β-methoxymethylcrotonate (6·5 g.) was added in one portion. The product was worked up as for γ-methoxy-β-methylcrotonic acid. The solid residue of *γ-methoxy-β-methoxymethylcrotonic acid* crystallised from water in needles, m. p. 83° (Found: C, 52·8; H, 7·3%; equiv., 161. $C_7H_{12}O_4$ requires C, 52·5; H, 7·55%; equiv., 160), $\lambda_{max.}$ 212 mμ (ε 8400) [*4-phenylphenacyl ester* (from aqueous ethanol), m. p. 110° (Found: C, 70·8; H, 6·2. $C_{21}H_{22}O_5$ requires C, 71·15; H, 6·25%)].

Methyl γ-Methoxycrotonate.—Methyl γ-bromocrotonate (18 g.) and calcium carbonate (10 g.) in methanol (50 c.c.), refluxed for 7 days, gave methyl γ-methoxycrotonate (7·9 g., 67%), b. p. 76—78°/12 mm., n_D^{28} 1·4380, hydrolysed to the acid, m. p. 66—67° (4-phenylphenacyl ester, m. p. 109°).

Methyl αγ-Dibromo-β-methylcrotonate.—Methyl α-bromo-β-methylcrotonate (85 g.) and bromosuccinimide (82·5 g.) in carbon tetrachloride (250 c.c.) containing benzoyl peroxide (0·5 g.) on a water-bath for 1½ hr. gave *methyl αγ-dibromo-β-methylcrotonate* (102 g., 83%), b. p. 76—80°/3·2 × 10^{-3} mm., n_D^{29} 1·5379—1·5415 (Found: C, 26·5; H, 2·85; Br, 58·0. $C_6H_8O_2Br_2$ requires C, 26·5; H, 2·95; Br, 58·75%). After a few days the last ester fraction deposited needles (0·4 g.); these recrystallised in prisms, m. p. 64—65° (see below), from carbon tetrachloride.

Methyl α-Bromo-γ-methoxy-β-methylcrotonate.—Methyl αγ-dibromo-β-methylcrotonate (64 g.) with calcium carbonate (23 g.) in methanol (400 c.c.) for 7 days gave *methyl α-bromo-γ-methoxy-β-methylcrotonate* (35·4 g., 71%), b. p. 89—93°/7 mm., n_D^{27} 1·4860—1·4875 (Found: C, 37·7; H, 4·8; Br, 35·5. $C_7H_{11}O_3Br$ requires C, 37·7; H, 5·0; Br, 35·8%), $\lambda_{max.}$ 243 mμ (ε 3650).

The distillation residue (9 g.) solidified and crystallised from carbon tetrachloride in needles,

[20] Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 4279; Veeravagu, M.Sc. Thesis, University of Ceylon, 1956.

m. p. 64—65°, identical (mixed m. p.) with the solid obtained as in the preceding paragraphs. It was lactonic and was formulated as *α-bromo-γ-hydroxy-β-methylcrotonic acid lactone* (Found: C, 33·9; H, 2·85; Br, 45·15. $C_5H_5O_2Br$ requires C, 33·9; H, 3·1; Br, 45·2%), $\lambda_{max.}$ 226 mμ (ε 9400), $\nu_{max.}$ (in Nujol) 1739, 1770 (C=O), 1639 (C=C), 1376, 1456 (CH deformation, *C*-Me), 2899 (CH stretching, *C*-Me) cm.$^{-1}$ (the authors thank Mr. R. L. Erskine, B.Sc., A.R.C.S., Imperial College, London, for these data).

Ozonolysis of Methyl α-Bromo-γ-methoxy-β-methylcrotonate.—The bromo-ester (1·0 g.) in carbon tetrachloride (15 c.c.) was ozonised at 0°. The carbon tetrachloride was removed and the ozonide was mixed with glacial acetic acid (10 c.c.) and zinc dust (0·5 g.) and steam-distilled. The distillate gave an orange methoxyacetone 2,4-dinitrophenylhydrazone which, purified by chromatography on an alumina column with benzene–light petroleum (b. p. 60—80°) and crystallised from methanol, had m. p. and mixed m. p. 165°. The aqueous residue in the steam-distillation flask was acidified (Congo Red) and extracted with ether for 4 days. The dried extract on evaporation gave oxalic acid dihydrate, m. p. and mixed m. p. 100—101°.

Methyl αγ-Dibromocrotonate.—Methyl α-bromocrotonate (52 g.) and *N*-bromosuccinimide (55 g.) in carbon tetrachloride (150 c.c.) containing benzoyl peroxide (0·3 g.) on a water-bath gave, in 22 hr., *methyl αγ-dibromocrotonate* (67 g., 90%), b. p. 81—86°/0·8 mm., n_D^{30} 1·5402 (Found: C, 23·3; H, 2·54; Br, 62·3. $C_5H_6O_2Br_2$ requires C, 23·3; H, 2·35; Br, 62·0%).

Methyl α-Bromo-γ-methoxycrotonate.—Methyl αγ-dibromocrotonate (65 g.), when refluxed with calcium carbonate (25 g.) in methanol (400 c.c.) for 8 days, gave *methyl α-bromo-γ-methoxycrotonate*, b. p. 63—67°/10^{-3} mm., n_D^{28} 1·4830 (Found: C, 34·0; H, 4·2; O, 23·1; Br, 39·3. $C_6H_9O_3Br$ requires C, 34·45; H, 4·35; O, 23·0; Br, 38·2%. A second analysis also gave a high Br value), $\lambda_{max.}$ 233 mμ (ε 6100).

Attempts to lactonise Methyl αγ-Dibromo-β-methylcrotonate.—The bromo-ester (1·0 g.), when heated in carbon tetrachloride, toluene (with or without benzoyl peroxide), xylene, anisole, dioxan, nitrobenzene, acetic acid, 50% sulphuric acid, or 48% hydrobromic acid (5 c.c.) at temperatures from 100° to 150° for 3—24 hr. gave 0—10% yields of lactone. When the ester (5 g.) had been refluxed with concentrated hydrochloric acid (20 c.c.) for 20 hr. and cooled, crystals (0·65 g.) of the lactone, m. p. 63°, were filtered off and the filtrate was continuously extracted with ether. Evaporating the dried extracts gave a yellow oil (2·50 g.).

Methyl γ-Bromo-β-phenylcrotonate.—Methyl β-phenylcrotonate [21] (9·0 g.) and benzoyl peroxide (0·15 g.) in carbon tetrachloride (25 c.c.) were refluxed with *N*-bromosuccinimide (9·5 g.) in carbon tetrachloride (30 c.c.) for 18 hr. The product was isolated in the usual manner. *Methyl γ-bromo-β-phenylcrotonate* (8·7 g., 67%) had b. p. 100—102°/10^{-2} mm., n_D^{31} 1·5785 (Found: C, 51·35; H, 4·5; Br, 31·7. $C_{11}H_{11}O_2Br$ requires C, 51·8; H, 4·35; Br, 31·3%).

β-Phenylbutenolide.—Methyl γ-bromo-β-phenylcrotonate (1·0 g.) was refluxed with concentrated hydrochloric acid (5 c.c.) for 24 hr. (bath temp. 160—180°). The whole was cooled and extracted with ether; the extracts were dried (Na_2SO_4) and evaporated, giving β-phenylbutenolide (0·60 g., 91%), m. p. 94° (from water) (lit.,[4] m. p. 94°) (Found: C, 75·0; H, 5·1. Calc. for $C_{10}H_8O_2$: C, 75·0; H, 5·0%).

Methyl γ-Methoxy-β-phenylcrotonate.—Methyl γ-bromo-β-phenylcrotonate (3·2 g.), calcium carbonate (1·30 g.), and dry methanol (5 c.c.) were refluxed for 6 days and the product was worked up in the usual manner. *Methyl γ-methoxy-β-phenylcrotonate* (2·0 g., 77%) distilled at 121—122°/7 mm. and had n_D^{30} 1·5410 (Found: C, 69·1; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%), $\lambda_{max.}$ 206 (ε 15,000), 264 (ε 10,300), 268 (ε 12,000), and 273 mμ (ε 11,000).

γ-Methoxy-β-phenylcrotonic Acid.—The ester (3·02 g.) was kept in aqueous N-sodium hydroxide (50 c.c.) and methanol (10 c.c.) at 95° for 8 min., then cooled, acidified, and extracted with ether. The extracts were dried (Na_2SO_4) and evaporated. The residue on distillation gave a liquid acid (2·85 g.), b. p. 150—151°/3 mm., n_D^{31} 1·5660 (Found: C, 68·65; H, 6·5. Calc. for $C_{11}H_{12}O_3$: C, 68·7; H, 6·3%), $\lambda_{max.}$ 205 (ε 13,600), 214 (ε 14,800), 261 (ε 11,300), 265 (ε 14,800) and 267 mμ (ε 11,300), giving a faint precipitate with Brady's reagent and therefore containing a small amount (<10%) of the βγ-unsaturated acid (see below).

This liquid acid, on storage, deposited *γ-methoxy-β-phenylcrotonic acid*, m. p. 54° [colourless needles from light petroleum (b. p. 60—80°)] (Found: C, 68·5; H, 6·35%), $\lambda_{max.}$ 206 (ε 15,600), 213 (infl. ε 11,900), 260 (ε 14,600), and 263 mμ (ε 13,400) (cf. ref. 22).

Ethyl γ-Bromo-α-cyano-β-methylcrotonate.—Ethyl α-cyano-β-methylcrotonate (8 g.) in carbon

[21] Lipkin and Stewart, *J. Amer. Chem. Soc.*, 1939, **61**, 3295.
[22] Braude, *Ann. Reports*, 1945, **42**, 126.

tetrachloride (30 c.c.) was refluxed with *N*-bromosuccinimide (9·5 g.) and benzoyl peroxide (0·15 g.) for 2 hr. and the product worked up in the usual manner. *Ethyl γ-bromo-α-cyano-β-methylcrotonate* had b. p. 69—70°/8 × 10^{-3} mm., n_D^{31} 1·5100 (9·2 g., 75·8%) (Found: C, 41·15; H, 4·65; Br, 34·9. $C_8H_{10}O_2NBr$ requires C, 41·40; H, 4·35; Br, 34·4%).

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