95. *Olefinic Acids. Part I. The Reactivity of α-Bromocrotonic Acid.*

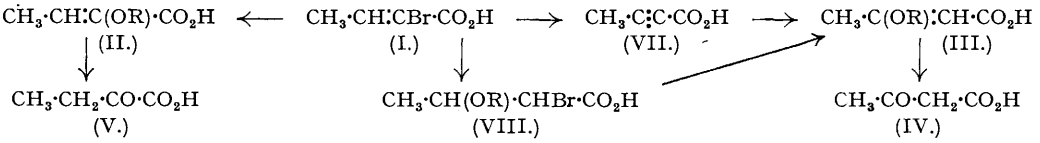
By L. N. Owen.

The halogen atom in α-bromocrotonic acid is sufficiently reactive to yield the hitherto unknown *α-methoxy-* and *α-ethoxy-crotonic acids* when treated with the appropriate sodium alkoxide or alcoholic alkali. The simultaneous formation of β-alkoxycrotonic acids has been observed, and with *iso*propanol and *tert.*-butanol the main products are β-iso*propoxycrotonic acid* and β-tert.-*butoxycrotonic acid*. The mechanism of the reaction is discussed, and the absorption spectra of the compounds, which show characteristic differences in the α- and β-series, are recorded.

The halogen atom in α-chlorocrotonic acid is known to be remarkably stable; the acid cannot be converted into tetrolic acid, and is unaffected by boiling alcoholic potash or sodium ethoxide at 215° (Sarnow, *Annalen*, 1872, **164**, 96; Kahlbaum, *Ber.*, 1879, **12**, 2338; Friedrich, *Annalen*, 1883, **219**, 322). Apart from a brief statement by Michael and Pendleton (*J. pr. Chem.*, 1888, **38**, 1) to the effect that α-bromocrotonic acid " loses hydrogen bromide " when heated with dilute alkali, the only indication of the greater reactivity of the bromo-acid is to be found in the recent observation of Backer and Oosten (*Rec. Trav. chim.*, 1940, **59**, 41), who have shown that it may be converted into α-arsonocrotonic acid by treatment with sodium arsenite. Before the latter paper was available, the present author had noted the reactivity of α-bromocrotonic acid towards alcoholic alkali, and a further investigation was thought to be desirable.

α-Bromocrotonic acid (I) was unaffected by cold sodium alkoxides, but on boiling with an excess of methanolic sodium hydroxide or sodium methoxide it gave crystalline *α-methoxycrotonic acid* (II; R = Me), accompanied by a small amount of β-methoxycrotonic acid (III; R = Me). The latter compound gave acetoacetic acid (IV), isolated as the 2 : 4-dinitrophenylhydrazone, on cold acid hydrolysis. The structure of (II; R = Me) was confirmed by the following observations: (i) On hydrogenation it was smoothly converted into α-methoxybutyric acid (p-*phenylphenacyl* ester, m. p. 82°), (ii) α-ketobutyric acid (V) was obtained by acid hydrolysis, and (iii) acetaldehyde and oxalic acid were formed on ozonisation. The necessity of establishing the position

of the ethylenic linkage in this acid was emphasised when it was found that α-bromo-ββ-dimethylacrylic acid on treatment with sodium methoxide yielded mainly α-methoxy-β-methylenebutyric acid (the experimental evidence for this *iso*propylidene–*iso*propenyl isomerisation will be given in a later paper in this series).



α-Bromo*iso*crotonic acid underwent a similar reaction, though less readily, longer heating being necessary for complete removal of the halogen. The α-methoxycrotonic acid so prepared was identical with that described above, and it was also obtained directly from αβ-dibromobutyric acid. This would be anticipated from the known transformation of the latter acid into a mixture of α-bromocrotonic and α-bromo*iso*crotonic acids by treatment with alkali (*inter alia*, James, J., 1910, **97**, 1565).

By similar procedures, crystalline *α-ethoxycrotonic acid* was prepared, but it was accompanied by a considerable quantity of β-ethoxycrotonic acid. This increased yield of the β-derivative made it of interest to extend the reaction to higher alkoxides, and it was found that potassium *iso*propoxide gave mainly *β-isopropoxycrotonic acid*; only a small amount of the *α-isomer* was formed. With potassium *tert.*-butoxide, the sole product appeared to be β-tert.-*butoxycrotonic acid*. The latter substance was also obtained, though in very small yield, from α-chlorocrotonic acid.

There are two possible routes by which the formation of β-alkoxycrotonic acids (III) may be envisaged. The α-bromocrotonic acid (I) may suffer loss of hydrogen bromide to give tetrolic acid (VII), from which (III) might be formed by addition of alcohol. Alternatively, (I) may react additively with the alcohol to give an α-bromo-β-alkoxybutyric acid (VIII), which by loss of hydrogen bromide could give (III). Feist (*Annalen*, 1906, **345**, 104) suggested that tetrolic acid is capable of undergoing addition of alcohol, and it has now been shown that this does occur very readily; β-methoxy- and β-*tert.*-butoxy-crotonic acids were prepared by this method. The second mechanism is supported by the observation that synthetic *α-bromo-β-ethoxybutyric acid* gives a high yield of β-ethoxycrotonic acid when heated with alcoholic potassium hydroxide. Kögl, Veldstra, and Laan (*Annalen*, 1942, **552**, 1) have carried out a similar reaction with α-bromo-β-methoxybutyric acid.

Both routes are therefore possible insofar as the final stage is concerned, but it is more difficult to assess the relative probabilities of the transformation of (I) into (VII) or (VIII). The conversion of α-bromocrotonic acid into β-sulphocrotonic acid by the action of ammonium sulphite (Backer and Beute, *Rec. Trav. chim.*, 1935, **54**, 551) is most likely to occur by addition to the ethylenic linkage, followed by loss of hydrogen bromide, but this is of little significance in view of the readiness with which sulphites enter into addition reactions. Again, Carter and Ney (*J. Amer. Chem. Soc.*, 1942, **64**, 1223) have shown that ethyl α-bromocrotonate gives an excellent yield of ethyl α-bromo-β-methoxybutyrate when treated with sodium methoxide, but since addition is known to occur more readily to unsaturated esters than to unsaturated acids, this does not necessarily support the second mechanism. This difference in ease of addition is clearly indicated by the fact that, although the ester undergoes addition in preference to substitution, the acid, when reacting with sodium methoxide, gives mainly α-methoxycrotonic acid. The increased yield of the β-substituted derivative obtained with the higher alcohols is obviously significant, but little appears to be known of the relative reactivities of alcohols towards an ethylenic linkage. Beyerstedt and McElvain (*J. Amer. Chem. Soc.*, 1936, **58**, 529) have shown, however, that *tert.*-butanol does not react with keten acetal under conditions effective for ethanol; if this observation is of general application, it would appear that the second mechanism is the less probable. Attempts to interrupt the course of the reaction of α-bromocrotonic acid with alkoxides, in the hope of isolating one or both of the postulated intermediates, were not successful, and at present it is not possible to state whether one or both mechanisms are involved.

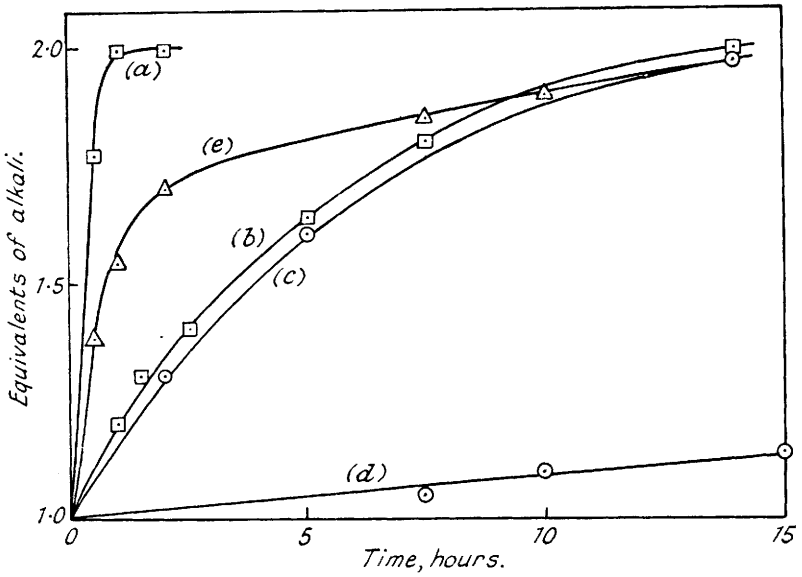
α-Methoxycrotonic acid reacted smoothly with diazomethane or with methyl iodide and silver oxide to yield *methyl α-methoxycrotonate*, characterised as the crystalline *amide*. It was hoped that it would be possible to cause this ester to undergo addition with alcohols, but it was quite inert towards cold or hot sodium methoxide solution, and was also unaffected by treatment with diazomethane; in the latter respect it resembles ethyl β-methoxycrotonate (Pechmann, *Ber.*, 1895, **28**, 1624). However, it reacted readily with methanolic hydrogen chloride, the methoxyl residue becoming attached in the α-position, to give *methyl αα-dimethoxybutyrate*, the structure of which was proved by hydrolysis to α-ketobutyric acid. These results are in harmony with the supposition that the influence normally exerted on the ethylenic linkage by the electron-attraction of the carboxyl group is overshadowed by the + *T* effect of the methoxyl group.

A difference in the relative reactivities of α-bromocrotonic acid and its *cis*-isomeride havng been observed with alcoholic alkali, it was then of interest to examine the effect of aqueous alkali. Michael and Pendleton (*loc. cit.*) observed that α-bromo*iso*crotonic acid was more resistant to this reagent than α-bromocrotonic acid, but did not investigate the products of the reaction. It has now been found that both acids are transformed into α-ketobutyric acid, though at very different rates (see Fig.). The results indicate that α-bromo*iso*crotonic acid may be freed from small amounts of its *trans*-isomer by treatment for one hour with an excess of N-alkali at 100°. Under these conditions the latter acid is completely converted into keto-acid, whereas only 20% of the former is destroyed. It was observed that a specimen of the *cis*-acid (m. p. 91°) was partly

isomerised on standing in a stoppered bottle, unprotected from light, for a year; the material then had m. p. 75—81°, and from its behaviour with alkali [Fig.; curve (*e*)] was evidently a mixture of *cis*- and *trans*-forms.

The facile decomposition of α-bromocrotonic acid with hot aqueous alkali is of importance in connection with the experiments of earlier workers on the elimination of hydrogen bromide from αβ-dibromobutyric acid and its esters. According to the majority of investigators (compare James, *loc. cit.*) the use of alkali hydroxides gives mainly α-bromo*iso*crotonic acid, m. p. 92°, but Ingold, Oliver, and Thorpe (J., **1924**, **125**, 2128) claimed that a quantitative yield of α-bromocrotonic acid, m. p. 106°, was obtained by boiling ethyl αβ-dibromobutyrate with aqueous alkali. In the light of the experiments already mentioned, it is evident that the *trans*-acid would not survive such treatment, and repetition of this saponification has shown that the main product is α-bromo*iso*crotonic acid, m. p. 92°, obtained in 65% yield.

The Action of Alkali on α-Bromocrotonic and α-Bromoisocrotonic Acids.



(*a*) α-Bromocrotonic acid in N-NaOH.
(*b*) ,, ,, ,, 0·1N-NaOH.
(*c*) α-Bromo*iso*crotonic acid in N-NaOH.
(*d*) α-Bromo*iso*crotonic acid in 0·1N-NaOH.
(*e*) Old specimen of α-bromo*iso*crotonic acid in N-NaOH.

The absorption data for the α- and β-alkoxycrotonic acids are shown in the table. The β-compounds absorb more strongly, and at longer wave-lengths, than their α-isomerides.

Light Absorption of Alkoxycrotonic Acids in Alcohol.

	$\lambda_{max.}$, A.	$\varepsilon_{max.}$		$\lambda_{max.}$, A.	$\varepsilon_{max.}$
α-Methoxy	2230	9400	β-Methoxy	2340	13,700
α-Ethoxy	2200	8700	β-Ethoxy	2320	14,600
α-*iso*Propoxy	2230	8100	β-*iso*Propoxy	2370	15,300
	2260 *	7700		2420 *	15,000
			β-*tert.*-Butoxy	2370	14,500
				2420 *	13,700

* Inflection.

Experimental.

(All solvents were removed under reduced pressure. Light petroleum, unless stated otherwise, refers to the fraction, b. p. 40—60°.)

α-Bromocrotonic acid, m. p. 106°, and α-bromo*iso*crotonic acid, m. p. 92°, were prepared from αβ-dibromobutyric acid, m. p. 87°, by the methods of Pfeiffer (*Ber.*, 1915, **48**, 1048) and James (J., 1910, **97**, 1572) respectively.

α-*Methoxycrotonic Acid.*—(i) To a solution of α-bromocrotonic acid (5·6 g.) in methanol (5 c.c.), methanolic potassium hydroxide (28 c.c., 3·76N) was added, and the mixture refluxed for 6 hours, the suspension of potassium α-bromocrotonate disappearing and being replaced by a granular precipitate of potassium bromide. After removal of solvent, the residue was dissolved in water and acidified with hydrochloric acid. A small amount (45 mg.) of β-methoxycrotonic acid, m. p. 130°, was removed, and the filtrate extracted three times with ether. Evaporation of the dried extracts gave a solid residue (3·6 g.) of *α-methoxycrotonic acid*, which was readily soluble in water and the usual organic solvents, except light petroleum (b. p. 60—80°), from which it crystallised in needles, m. p. 58° (Found: C, 51·6; H, 6·9; equiv., 117. $C_5H_6O_3$ requires C, 51·7; H, 6·9%; equiv., 116). *Light absorption:* see Table. In another preparation, in which methanolic sodium methoxide was used in place of the potassium hydroxide, the acid was purified by distillation, b. p. 117°/16 mm., m. p. and mixed m. p. 58°. It rapidly decolourised bromine water and alkaline permanganate, and reacted slowly with aqueous 2 : 4-dinitrophenylhydrazine sulphate; after a week at room temperature the precipitate was collected and identified as the 2 : 4-dinitrophenylhydrazone of α-ketobutyric acid, m. p. 197° after recrystallisation from aqueous alcohol (Found: C, 42·6; H, 3·9; N, 20·4. Calc. for $C_{10}H_{10}O_6N_4$: C, 42·6; H, 3·6; N, 19·9%). Similar

treatment of β-methoxycrotonic acid gave the 2 : 4-dinitrophenylhydrazone of acetoacetic acid, m. p. 125° after crystallisation from ethyl acetate–light petroleum (compare Clift and Cook, *Biochem. J.*, 1932, **26**, 1800) (Found : N, 20·7. Calc. for $C_{10}H_{10}O_6N_4$: N, 19·9%).

(ii) The use of α-bromo*iso*crotonic acid (1·5 g.) in place of α-bromocrotonic acid, with the corresponding amount of sodium methoxide solution, necessitated a prolongation of the period of refluxing to 20 hours. Sodium bromide began to separate from the clear reaction mixture (sodium α-bromo*iso*crotonate is readily soluble in methanol) only after 3 hours' heating. The α-methoxycrotonic acid obtained was identical with that described above, m. p. and mixed m. p. 58°. No β-methoxycrotonic acid was encountered, possibly owing to the small scale of the experiment.

(iii) αβ-Dibromobutyric acid (2·0 g.), m. p. 87°, dissolved in dry methanol (5 c.c.), was treated with methanolic sodium methoxide (7 c.c., 4N) and refluxed for 20 hours. After working up as before, α-methoxycrotonic acid (0·6 g.) was isolated, m. p. and mixed m. p. 57—58°. No β-methoxycrotonic acid was detected.

Ozonisation.—α-Methoxycrotonic acid (0·5 g.), dissolved in carbon tetrachloride (5 c.c.), was ozonised in the usual manner, the issuing gases being led through water, this water subsequently being shown to contain no appreciable quantity of formaldehyde (dimedone test). An oily ozonide separated during the reaction, and after removal of solvent it was steam-distilled. Acetaldehyde was detected in the distillate (2 : 4-dinitrophenylhydrazone, m. p. 164°), and evaporation to dryness of the still residue furnished oxalic acid (0·3 g., anhydrous), m. p. 188°.

Hydrogenation.—A solution of α-methoxycrotonic acid (1·44 g.) in water (10 c.c.) was shaken in hydrogen with a palladium–charcoal catalyst (0·2 g., 10%); the absorption of gas amounted to 99·2% of the theoretical in 1½ hours. The α-methoxybutyric acid (1·15 g.) so obtained had b. p. 94—95°/15 mm., $n_D^{19°}$ 1·4202, and was characterised as the p-*phenylphenacyl* ester, m. p. 82°, unchanged on admixture with a specimen prepared from authentic α-methoxybutyric acid (Found : C, 72·7; H, 7·0; OMe, 9·5. $C_{19}H_{20}O_4$ requires C, 73·0; H, 6·5; OMe, 9·9%).

Hydrolysis.—α-Methoxycrotonic acid (1·0 g.) in sulphuric acid (5 c.c., 2N) was heated in a distillation flask on the steam-bath for 1 hour. The few drops of distillate gave a strong positive Denigès test for methanol. The residual solution was extracted with ether, and the α-ketobutyric acid (0·6 g.) obtained by evaporation of the dried extracts, distilled at b. p. 78°/16 mm. It was characterised by preparation of the oxime, m. p. 157°, the *p*-nitrophenylhydrazone, m. p. 206°, and the 2 : 4-dinitrophenylhydrazone, m. p. 195°.

Methyl α-Methoxycrotonate.—α-Methoxycrotonic acid (2·0 g.) was dissolved in methyl iodide (5 c.c.) and treated with dry silver oxide (5 g.) in small portions, with cooling. After standing at room temperature for an hour, with occasional shaking, dry ether was added, the silver salts removed, and the solvent evaporated. The *ester* distilled smoothly as a colourless mobile oil, b. p. 161°/762 mm., 64°/16 mm., $n_D^{18°}$ 1·4385. *Light absorption :* $\lambda_{max.}$ 2200 A. (ε 8450), 2235 A. (ε 8450) (Found : C, 55·6; H, 8·3. $C_6H_{10}O_3$ requires C, 55·35; H, 7·75%). It rapidly decolourised bromine water and alkaline permanganate. With concentrated aqueous ammonia it gave *α-methoxycrotonamide*, long needles from ether, m. p. 101—102° (Found : C, 52·3; H, 8·0; N, 11·9. $C_5H_9O_2N$ requires C, 52·1; H, 7·9; N, 12·2%). The same ester was also prepared, and characterised as the amide, by the treatment of α-methoxycrotonic acid with ethereal diazomethane; the use of a large excess of diazomethane, for a period of 2 days at 15—20°, gave the same product.

The ester was recovered unchanged after treatment in dry methanol with sodium methoxide, either for 2 days at 20° or for 7 hours under reflux, but when a cooled solution in dry methanol (1 g. in 4 c.c.) was saturated with dry hydrogen chloride, the reducing power disappeared. After standing for 1 hour at 10°, the hydrogen chloride was removed by aeration, and finally by neutralisation with silver carbonate. Evaporation of the filtrate afforded *methyl αα-dimethoxybutyrate* (0·4 g.), b. p. 77°/16 mm., $n_D^{20°}$ 1·4192, which was stable towards bromine water (Found : C, 51·4; H, 8·6. $C_7H_{14}O_4$ requires C, 51·8; H, 8·7%). When heated with dilute sulphuric acid, it gave α-ketobutyric acid (2 : 4-dinitrophenylhydrazone, m. p. 196°).

Reactions of α-Bromocrotonic Acid with Other Alkoxides.—(i) To a solution of the bromo-acid (1·5 g.) in ethanol (2 c.c.), ethanolic sodium ethoxide (15 c.c., 2N) was added (alternatively, ethanolic potassium hydroxide may be used). After refluxing for 5 hours, the solvent was removed, and the residue, dissolved in water, acidified with dilute sulphuric acid. β-Ethoxycrotonic acid rapidly separated, and was collected, washed with water, and dried (yield, 0·5 g.). It crystallised from aqueous methanol in needles, m. p. 140°. *Light absorption :* see Table (Found : C, 55·6; H, 7·9. Calc. for $C_6H_{10}O_3$: C, 55·35; H, 7·75%). On standing at 20° with aqueous 2 : 4-dinitrophenylhydrazine sulphate it slowly gave a yellow precipitate of acetoacetic acid 2 : 4-dinitrophenylhydrazone, m. p. 125°. The filtrate from which the β-ethoxycrotonic acid had been separated was extracted with ether and gave *α-ethoxycrotonic acid* (0·45 g.), needles from light petroleum, m. p. 46—47°. *Light absorption :* see Table. (Found : C, 55·6; H, 7·8. $C_6H_{10}O_3$ requires C, 55·35; H, 7·75%). The acid was readily soluble in water and organic solvents. With aqueous 2 : 4-dinitrophenylhydrazine sulphate it afforded the 2 : 4-dinitrophenylhydrazone of α-ketobutyric acid, m. p. 195°.

(ii) Potassium *iso*propoxide in dry *iso*propanol (30 c.c., 2·5N) was added to a solution of α-bromocrotonic acid (5·0 g.) in dry *iso*propanol (5 c.c.). The mixture was refluxed for 10 hours, evaporated to dryness, and the residue, dissolved in water, was acidified with hydrochloric acid. The precipitate was collected, washed with water, and dried (yield, 2·8 g.); this β-iso*propoxycrotonic acid*, which was insoluble in cold water, crystallised from methanol in large irregular prisms, m. p. 106° (Found : C, 58·4; H, 8·3. $C_7H_{12}O_3$ requires C, 58·3; H, 8·4%). *Light absorption :* see Table. On warming with dilute sulphuric acid it gave acetone (2 : 4-dinitrophenylhydrazone, m. p. 128°). Extraction of the original filtrate with ether, and distillation of the product, gave slightly impure α-iso*propoxycrotonic acid* (0·6 g.), b. p. 110—112°/10 mm., $n_D^{16°}$ 1·4530, which still contained traces of halogen (Found : C, 57·7; H, 8·2. $C_7H_{12}O_3$ requires C, 58·3; H, 8·4%). *Light absorption :* see Table. On acid hydrolysis it gave α-ketobutyric acid (2 : 4-dinitrophenylhydrazone, m. p. 197°).

(iii) A solution of potassium *tert.*-butoxide in *tert.*-butanol (75 c.c., N) was added to α-bromocrotonic acid (5·0 g.) dissolved in warm *tert.*-butanol (10 c.c.). The mixture was refluxed for 30 hours, and the residue, after removal of solvent, was dissolved in water and acidified with hydrochloric acid. The precipitate was collected, washed with water, and dried (yield, 1·5 g.); this β-tert.-*butoxycrotonic acid* crystallised from methanol in large needles, m. p. 127° (Found : C, 60·5; H, 9·0. $C_8H_{14}O_3$ requires C, 60·7; H, 8·9%). *Light absorption :* see Table. On warming with dilute sulphuric acid it gave acetone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 128°). The original filtrate was extracted with ether, which on evaporation yielded a solid residue of unchanged α-bromocrotonic acid (1·8 g.), m. p. and mixed m. p. 106°, after recrystallisation from water.

Reactions of Tetrolic Acid and Alkoxides.—(i) Sodium methoxide in methanol (1·5 c.c., 4N) was added to a solution of tetrolic acid (0·25 g.) in methanol (2 c.c.). After refluxing for 4 hours, the solvent was removed, and the residue dissolved in water. Acidification with hydrochloric acid gave a precipitate of β-methoxycrotonic acid (0·25 g.), m. p. 130° after recrystallisation from water. *Light absorption :* see Table. (Larger quantities of this acid cannot be crystallised from water without considerable loss by decomposition.)

(ii) Tetrolic acid (0·5 g.) was refluxed for 20 hours with a solution of potassium *tert.*-butoxide in *tert.*-butanol (10 c.c., N). Solvent was then removed, and the residue dissolved in water and acidified with hydrochloric acid. The precipitated β-*tert.*-butoxycrotonic acid (70 mg.), recrystallised from methanol, formed needles, m. p. and mixed m. p. 127°.

Action of Potassium tert.-*Butoxide* on *α-Chlorocrotonic Acid.*—The chloro-acid (0·7 g.), m. p. 99°, was refluxed for 30 hours with the reagent (15 c.c., N). On working up the product as described above, *β-tert.*-butoxycrotonic acid (60 mg.) was obtained, m. p. 126°.

α-Bromo-β-ethoxybutyric Acid.—This was synthesised by the method described by West, Krummel, and Carter (*J. Biol. Chem.*, 1938, **122**, 605) for the preparation of the bromo-methoxy-acid. Crotonic acid (26 g.) gave a crude solid (32 g.), which, when recrystallised from light petroleum (b. p. 60—80°), yielded large prisms of *α-bromo-β-ethoxybutyric acid*, m. p. 75° (Found : C, 33·9; H, 5·3; Br, 38·4; equiv., 211. $C_6H_{11}O_3Br$ requires C, 34·1; H, 5·3; Br, 37·9%; equiv., 211). The *methyl* ester, prepared by the use of ethereal diazomethane, had b. p. 78°/10 mm., $n_D^{14°}$ 1·4512 (Found : C, 37·7; H, 6·1. $C_7H_{13}O_3Br$ requires C, 37·35; H, 5·8%).

Treatment of the acid (5·0 g.) with boiling ethanolic sodium ethoxide (35 c.c., 2N) for 6 hours, yielded, after working up in the usual way, *β*-ethoxycrotonic acid (2·7 g., 88%), m. p. 140°.

*Action of Aqueous Alkali on α-Bromocrotonic and α-Bromo*iso*crotonic Acids.*—The results shown in the figure were obtained by heating the acid with 3 equivalents of N- or 0·1N-sodium hydroxide on the steam-bath (temperature of the solution, 95—97°), the reaction being followed by titration of samples with standard acid. The formation of α-keto-butyric acid in each experiment was shown by the preparation of the 2 : 4-dinitrophenylhydrazone, m. p. 197°, or the *p*-nitrophenylhydrazone, m. p. 206°.

Action of Aqueous Alkali on Ethyl αβ-Dibromobutyrate.—The ester (13·0 g., b. p. 107°/18 mm., prepared by the addition of bromine to ethyl crotonate in carbon tetrachloride), was heated on the steam-bath for 1 hour with 2N-sodium hydroxide (60 c.c.), with frequent shaking. Acidification of the cooled solution with hydrochloric acid gave α-bromo*iso*crotonic acid (3·2 g.), m. p. 92°, unchanged on recrystallisation from water. Extraction of the original filtrate with ether gave a further quantity of the same acid, which, when freed from a small amount of α-ketobutyric acid, amounted to 1·9 g., m. p. 92° after one recrystallisation from water.

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