191. *Olefinic Acids. Part II. The Reactivity of α-Bromoacrylic Acid and Some Related Compounds.*

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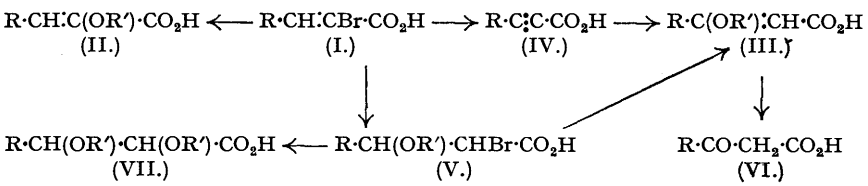
α-Bromoacrylic acid reacts with alkoxides to give α-bromo-β-alkoxy-propionic acids which, by further action, are converted into β-alkoxy-acrylic and αβ-dialkoxy-propionic acids, the proportion of β-alkoxy-acid being greater when the higher alkoxides are used. In contrast with the results obtained in the crotonic series (Part I), no α-alkoxy-acrylic acids are formed. Towards thioacetic acid, benzylthiol, diazomethane, and methyl diazoacetate, the order of decreasing reactivity is, as would be anticipated, α-bromoacrylic acid, α-bromocrotonic acid, α-bromo-ββ-dimethylacrylic acid; the products obtained by these addition reactions have been investigated and identified.

The absorption spectra of several α- and β-alkoxy-acrylic acids are recorded.

The investigations described in Part I (Owen, *J.*, 1945, 385) established that α-bromocrotonic acid (I; R = Me) reacted with alkoxides (or the appropriate alcoholic alkali) to give α- and β-alkoxy-crotonic acids, (II; R = Me) and (III; R = Me), the proportion of the latter being greater with the higher alkoxides, but attempts to isolate either of the possible intermediates (IV) or (V) were unsuccessful.



Baker (*J.*, 1942, 520) in the course of attempts to prepare α-alkoxy-acrylic acids, has shown that αβ-dibromopropionic acid, on treatment with boiling methanolic sodium methoxide, yields αβ-dimethoxypropionic acid, not by direct substitution, but probably *via* α-bromoacrylic acid. The presence of other products was indicated by the unsaturated nature of the crude halogen-free acids isolated from the reaction mixture, but these were not identified, and the exact mechanism of the reaction was not established. It has now been found that *β-methoxyacrylic acid* is formed under these conditions; on cold acid hydrolysis it gives malonic semi-aldehyde (VI; R = H) (2 : 4-*dinitrophenylhydrazone*, m. p. 136°).

The reaction has been more closely studied by using α-bromoacrylic acid (I; R = H) as starting material, particularly with a view to comparing its behaviour with that of α-bromocrotonic acid. When boiled with methanolic sodium methoxide for 3 hours, the main product was α-bromo-β-methoxypropionic acid (V; R = H, R' = Me), which was isolated as its methyl ester, purified from unsaturated compounds by cautious treatment with aqueous permanganate, and characterised as the amide, m. p. 83°. The presence also of a small amount of β-methoxy-acrylic acid (III; R = H, R' = Me) was demonstrated by the formation of malonic semi-aldehyde by acid hydrolysis of a portion of the reaction products. No α-methoxyacrylic acid could be detected, but, clearly, if it had been formed it might well have been converted by subsequent reaction with methanol into αβ-dimethoxypropionic acid. This, however, has been shown not to be the case, since, by saponification of methyl α-methoxyacrylate, crystalline *α-methoxyacrylic acid*, m. p. 52°, was obtained,* which was recovered unchanged after treatment with boiling methanolic sodium methoxide; β-methoxyacrylic acid, treated similarly, was likewise unaffected.

It is evident, therefore, that α-bromoacrylic acid, in marked contrast to α-bromocrotonic acid, undergoes addition, rather than substitution, and gives the bromomethoxy-acid (V; R = H, R' = Me), the bromine atom in which is then either eliminated as hydrogen bromide, forming β-methoxyacrylic acid (III; R = H, R' = Me), or replaced to give αβ-dimethoxy-propionic acid (VII; R = H, R' = Me).

It was not possible to interrupt the reaction of α-bromoacrylic acid with ethanolic alkali at the bromo-ethoxy-acid stage, probably owing to the heterogeneous nature of the reaction mixture resulting from the reduced solubility of the salts in ethanol, but on taking the reaction to com-

* Allpress and Haworth (*J.*, 1924, **125**, 1233) tentatively ascribed this structure to an unsaturated liquid acid, b. p. 65—75°/12 mm., obtained by the action of methyl chloroformate on fructose; it is possible that their product was an impure form of α-methoxyacrylic acid, although no other properties were given in support of the proposed constitution.

pletion β-ethoxyacrylic acid was obtained, together with αβ-diethoxypropionic acid, isolated as the *ethyl* ester. Treatment of α-bromoacrylic acid with potassium *iso*propoxide gave a liquid product, containing 88% of β-iso*propoxyacrylic acid* with 12% of αβ-di*iso*propoxypropionic acid, which could not be separated, whilst with potassium *tert.*-butoxide the only product isolated was crystalline β-tert.-*butoxyacrylic acid.* This progressive increase in the proportion of the β-alkoxy-acid as the higher alkoxides are used is similar to that observed in the case of α-bromocrotonic acid; in the present reactions, however, the increase is at the expense of dialkoxypropionic acid, whilst in the crotonic series it is accompanied by a diminution in the amount of α-alkoxy-acid.

The absorption data for the α- and β-alkoxy-acrylic acids are shown in the table. As was observed in the crotonic series (Owen, *loc. cit.*) the β-compounds absorb more strongly than their α-isomerides, but in contrast, not at appreciably different wave-lengths.

Light Absorption of Alkoxy-acrylic Acids in Alcohol.

	$\lambda_{max.}$, A.	$\epsilon_{max.}$		$\lambda_{max.}$, A.	$\epsilon_{max.}$
α-Methoxy	2280	6000	β-Methoxy	2280	14,100
α-Ethoxy *	2290	7000	β-Ethoxy	2300	14,700
	2360 †	6150			
			β-*iso*Propoxy	2340	14,000 ‡
			β-*tert.*-Butoxy	2370	15,400

* M. p. 61°, prepared by the method of Claisen (*Ber.*, 1898, **31**, 1019; cf. von Auwers, *ibid.*, 1911, **44**, 3524).

† Inflection. ‡ Corrected value.

The greater ease of addition to α-halogeno-acrylic, as compared with α-halogeno-crotonic, acids has also been demonstrated in their reactions with a number of other reagents. α-Bromoacrylic acid reacted readily with thioacetic acid to give α-*bromo*-β-(*acetylthio*)*propionic acid* (VIII); the corresponding *chloro*-acid was obtained similarly. α-Bromocrotonic acid failed to undergo addition of the reagent, thus indicating that diminution of ethenoid activity is brought about not only by the methyl group in the β-position, but also by the halogen atom, since crotonic acid undergoes the reaction (Holmberg and Schjanberg, *Arkiv Kemi, Min. Geol.*, 1940, **14** *A*, No. 7, 22).

With benzylthiol in pyridine solution, α-bromoacrylic acid gave β-(*benzylthio*)*acrylic acid* (IX), presumably *via* the intermediate compound (X); α-bromocrotonic acid could not be induced to react with the reagent.

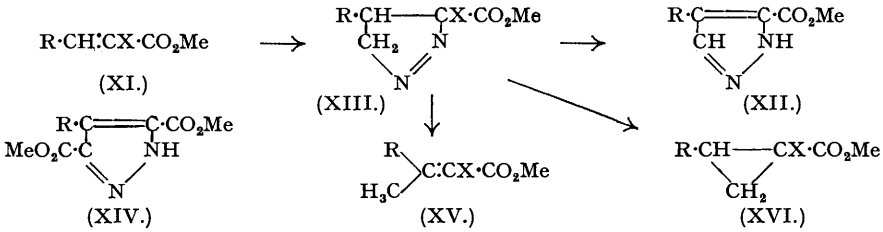
$CH_2(SAc)\cdot CHBr\cdot CO_2H$ (VIII.) $CH_2(SBz)\cdot CHBr\cdot CO_2H$ (X.) $CH(SBz):CH\cdot CO_2H$ (IX.)

Auwers and König (*Annalen*, 1932, **496**, 31) reported that methyl α-chlorocrotonate (XI; R = Me, X = Cl) reacted with diazomethane to give methyl 4-methylpyrazole-3-carboxylate (XII; R = Me), hydrogen chloride being spontaneously evolved by the unstable intermediate (XIII; R = Me, X = Cl). It has now been shown that α-chloro- and α-bromo-acrylic acids, on treatment with diazomethane, give methyl pyrazole-3-carboxylate (XII; R = H), whilst α-bromocrotonic acid gives (XII; R = Me). α-Bromo-ββ-dimethylacrylic acid, on the contrary, was merely converted into its *methyl* ester (*amide*, m. p. 129°) and did not undergo addition, the extra methyl group in the β-position being sufficient to inhibit the reaction.

Buchner and Papandieck (*Annalen*, 1893, **273**, 246), by treatment of methyl αβ-dibromopropionate with methyl diazoacetate, obtained dimethyl pyrazole-3 : 5-dicarboxylate (XIV; R = H), but did not isolate any of the intermediates. Both methyl α-bromo- and α-chloroacrylate have now been found to give this product under these conditions, whilst methyl α-bromo- and α-chloro-crotonates reacted much less readily, and gave a small yield of *methyl 4-methylpyrazole-3 : 5-dicarboxylate* (XIV; R = Me). Methyl α-bromo-ββ-dimethylacrylate was unaffected by methyl diazoacetate.

In the reaction of diazomethane with α-substituted acrylic or crotonic esters (XI), provided that the intermediate pyrazoline (XIII) does not tend to lose HX and form pyrazoles (cf. above), it may lose nitrogen to give either a higher homologue (XV) of the ester (XI) or a *cyclo*propane derivative (XVI). The composition of the product depends on the nature of the substituent X; if it is methyl, both (XV)and (XVI) are obtained, whilst if X is a cyano- or carbalkoxy-group the sole product is (XV) (Auwers and König, *Annalen*, 1932, **496**, 252; Young, Andrews, Lindenbaum, and Cristol, *J. Amer. Chem. Soc.*, 1944, **66**, 810). It was therefore not unexpected to find that methyl α-methoxyacrylate (XI; R = H, X = OMe) on reaction with diazomethane

gave a product which contained methyl 1-methoxy*cyclo*propane-1-carboxylate (XVI; R = H, X = OMe), characterised as the *amide*, m. p. 117°. This $+T$ effect of the methoxyl group in the α-position was also shown by the observation that although, as mentioned above, methyl α-methoxyacrylate was unaffected by methanolic sodium methoxide, it reacted with methanolic hydrogen chloride to give methyl αα-dimethoxypropionate.



Experimental.

Action of Sodium Methoxide on αβ-Dibromopropionic Acid.—To the acid (24 g.) in warm methanol (20 c.c.) was added methanolic sodium methoxide (110 c.c., 3·76 N). After the vigorous reaction had subsided, the mixture was refluxed for 7 hours, during which the suspension of potassium α-bromoacrylate disappeared and was replaced by a granular precipitate of potassium bromide. After removal of solvent, the residue was dissolved in water and acidified with hydrochloric acid, with ice-cooling. Extraction with ether gave a syrup, which partly crystallised on standing. The solid *β-methoxyacrylic acid* (1·1 g.) was dried on porous tile; it recrystallised from water in plates, m. p. 102° (Found: C, 47·2; H, 5·9; equiv., 102. $C_4H_6O_3$ requires C, 47·1; H, 5·9%; equiv., 102). Light absorption: see Table. On treatment with a cold solution of 2 : 4-dinitrophenylhydrazine sulphate in 5N-sulphuric acid for 2 hours it gave the 2 : 4-*dinitrophenylhydrazone* of malonic semi-aldehyde, which crystallised from warm ethyl acetate–light petroleum (b. p. 40—60°) in lemon-yellow nodules, m. p. 136° (decomp.), and gave a deep red solution in aqueous sodium hydroxide (Found: C, 40·0; H, 3·3; N, 20·6. $C_9H_8O_6N_4$ requires C, 40·3; H, 3·0; N, 20·9%).

α-Bromoacrylic Acid.—*αβ*-Dibromopropionic acid (90 g.) was dissolved in water and neutralised with N-sodium hydroxide at 0°. An equal volume of N-sodium hydroxide was then added and the solution left at room temperature for 1 hour. After acidification with a slight excess of concentrated hydrochloric acid (Congo-red), ether extraction yielded α-bromoacrylic acid, which after recrystallisation from light petroleum (b. p. 60—80°) formed colourless prisms (51 g., 87%), m. p. 72° (lit. 70°). This improved procedure gives a product which, unlike less pure material, shows no sign of decomposition after being kept for several months.

Reaction of α-Bromoacrylic Acid with Alkoxides.—(i) A solution of the acid (15 g.) in methanol (40 c.c.) was treated with methanolic sodium methoxide (35 c.c., 3·67N) and refluxed for 3 hours, after which it was evaporated to dryness, and the residue dissolved in water, acidified with hydrochloric acid, and extracted with ether. The liquid acid so obtained contained a small amount of β-methoxyacrylic acid, since a portion, on treatment with aqueous 2 : 4-dinitrophenylhydrazine sulphate, gave the 2 : 4-dinitrophenylhydrazone of malonic semi-aldehyde, m. p. 135°. The remainder (7 g.) was dissolved in methyl iodide (5 c.c.) and diluted with ether (10 c.c.), and silver oxide (15 g.) was added in small portions during ½ hour. After refluxing for ½ hour, the solution was filtered and evaporated to an oil, which on distillation furnished a main fraction (6·1 g.), b. p. 70—78°/15 mm. This was unsaturated towards alkaline permanganate, and gave a positive reaction on standing with aqueous 2 : 4-dinitrophenylhydrazine sulphate. It was therefore suspended in dilute sodium carbonate solution and treated with a slight excess of 2% aqueous potassium permanganate at 0°, with vigorous stirring. The recovered saturated ester (3·0 g.), b. p. 78°/15 mm., $n_D^{19°}$ 1·4510, was mainly methyl α-bromo-β-methoxypropionate, probably containing a small amount of methyl αβ-dimethoxypropionate (Found: C, 33·4; H, 5·7. Calc. for $C_5H_9O_3Br$: C, 30·5; H, 4·6. Calc. for $C_6H_{12}O_4$: C, 48·6; H, 8·2%). On treatment with aqueous ammonia (*d* 0·880) it gave α-bromo-β-methoxypropionamide, m. p. 83° (Found: C, 26·2; H, 4·5. Calc. for $C_4H_8O_2NBr$: C, 26·4; H, 4·4%).

(ii) Ethanolic sodium ethoxide (45 c.c., 2N) was added to α-bromoacrylic acid (10 g.) in ethanol (10 c.c.) and the mixture was refluxed for 20 hours. The residue, after removal of solvent, was dissolved in water and acidified with hydrochloric acid, precipitating β-ethoxyacrylic acid (1·0 g.), which crystallised from warm water in plates, m. p. 109°. Light absorption: see Table. Ether extraction of the residual aqueous portion gave a liquid halogen-free acid (5·1 g.), which was esterified in the usual way in ethereal solution with ethyl iodide and silver oxide. The crude ester was then purified by treatment with 2% potassium permanganate, as already described, and on distillation gave *methyl αβ-diethoxypropionate* (1·5 g.), b. p. 87°/11 mm., $n_D^{21°}$ 1·4130 (Found: C, 56·8; H, 9·8. $C_9H_{18}O_4$ requires C, 56·8; H, 9·5%).

(iii) α-Bromoacrylic acid (7·5 g.), dissolved in *iso*propanol (60 c.c.), was treated with a solution of potassium (5 g.) in *iso*propanol (60 c.c.), and the semi-solid mass was refluxed for 24 hours on the steam-bath. The solvent was then removed, and the residue dissolved in water and acidified with hydrochloric acid; an oil separated, but since it could not be induced to crystallise, the whole was extracted with ether. The liquid acid so obtained (7 g.), b. p. 55°/0·001 mm., $n_D^{15°}$ 1·4425, contained no halogen and was highly unsaturated. Light absorption: $\lambda_{max.}$ 2340 A. (ε 12,300) (Found: equiv., 137. $C_6H_{10}O_3$ requires equiv., 130. $C_9H_{18}O_4$ requires equiv., 190). On treatment with aqueous 2 : 4-dinitrophenylhydrazine sulphate it gave the 2 : 4-dinitrophenylhydrazone of malonic semi-aldehyde, m. p. 129° (decomp.) after recrystallisation from dioxan, and was therefore mainly β-*iso*propoxyacrylic acid, probably containing

ca. 12% αβ-di*iso*propoxyacrylic acid. Attempts to isolate either component in a pure state were unsuccessful.

(iv) To a warm solution of potassium (10 g.) in *tert.*-butanol (200 c.c.) was added α-bromoacrylic acid (15·2 g.) in *tert.*-butanol (20 c.c.), and the semi-solid mass refluxed for 24 hours on the steam-bath. Water (100 c.c.) was then added and the *tert.*-butanol removed under reduced pressure. The residual aqueous solution was acidified to Congo-red with hydrochloric acid, which precipitated *β-tert.-butoxyacrylic acid* (3·2 g.); this was collected, and a further quantity (1·7 g.) obtained by extraction of the filtrate with ether. On recrystallisation from light petroleum (b. p. 60—80°) it formed long flat needles, m. p. 86·5° (Found: C, 58·6; H, 8·5; equiv., 144. $C_7H_{12}O_3$ requires C, 58·3; H, 8·4%; equiv., 144). Light absorption: see Table. On standing with aqueous 2 : 4-dinitrophenylhydrazine sulphate it gave the 2 : 4-dinitrophenylhydrazone of malonic semi-aldehyde, m. p. 131°. No other acidic products could be detected.

α-Methoxyacrylic Acid.—Methyl α-methoxyacrylate, b. p. 58—60°/15 mm., $\lambda_{max.}$ 2280 A. (ε 7300), $\lambda_{infl.}$ 2360 A. (ε 6400), was prepared by the method of Baker (*loc. cit.*). The ester (2·1 g.) was heated at 100° with aqueous sodium hydroxide (15 c.c., 2N) for 1½ hours, and the solution then cooled, acidified with 2N-hydrochloric acid (15 c.c.), and extracted with ether. Evaporation of the dried extract gave *α-methoxyacrylic acid* (1·2 g.), which crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 52° (Found: C, 46·8; H, 5·7. $C_4H_6O_3$ requires C, 47·0; H, 5·9%). Light absorption: see Table. On standing with aqueous 2 : 4-dinitrophenylhydrazine sulphate it gave the 2 : 4-dinitrophenylhydrazone of pyruvic acid, m. p. 218°.

Action of Sodium Methoxide on α-Methoxy- and β-Ethoxy-acrylic Acids.—α-Methoxyacrylic acid (0·2 g.) was refluxed with methanolic sodium methoxide (3 c.c., N) for 6 hours. After evaporation, acidification of the residue with hydrochloric acid and extraction with ether, the acid (0·17 g.), m. p. and mixed m. p. 50°, was recovered unchanged. β-Ethoxyacrylic acid (0·25 g.), treated similarly, was also recovered (0·21 g.), m. p. and mixed m. p. 108°.

α-Bromo-β-(acetylthio)propionic Acid.—α-Bromoacrylic acid (5 g.) was added in small portions to thioacetic acid (5 c.c.) in a flask cooled in ice. After the vigorous reaction had subsided, the solution was heated on the steam-bath for 15 minutes, and the excess of thioacetic acid then removed under reduced pressure. The solid *acid* obtained on cooling was recrystallised from carbon tetrachloride, from which it formed colourless prisms (6·9 g.), m. p. 85—86° (Found: C, 26·1; H, 3·2. $C_5H_7O_3SBr$ requires C, 26·4; H, 3·1%). Similar treatment of α-chloroacrylic acid (2 g.) afforded *α-chloro-β-(acetylthio)propionic acid* (3 g.), m. p. 75°, after recrystallisation from carbon tetrachloride (Found: C, 32·8; H, 3·75. $C_5H_7O_3ClS$ requires C, 32·9; H, 3·9%). Under the same conditions, α-bromocrotonic acid was recovered unchanged.

Action of Benzylthiol on α-Bromoacrylic Acid.—The acid (0·5 g.), pyridine (0·5 c.c.), and benzylthiol (1 c.c.) were heated on a steam-bath for 15 minutes. The solid which separated on cooling was freed from adhering oil on porous tile, dissolved in dilute hydrochloric acid, and extracted with ether. Removal of solvent yielded *β-(benzylthio)acrylic acid*, which crystallised from carbon tetrachloride in colourless plates, m. p. 162—163° (Found: C, 61·45; H, 5·3. $C_{10}H_{10}O_2S$ requires C, 61·8; H, 5·2%. Light absorption: $\lambda_{max.}$ 2740 A. (ε 15,500). Similar experiments, in which traces of hydrochloric acid or benzoyl peroxide were used in place of pyridine, resulted only in the recovery of unchanged bromo-acid.

Reactions of α-Halogeno-αβ-olefinic Acids with Diazomethane.—(i) α-Bromoacrylic acid (2 g.) was dissolved in excess of ethereal diazomethane and left at 20° for 5 days. After removal of solvent, the liquid residue was warmed to 60°, whereupon there was a vigorous evolution of hydrogen bromide and the formation of methyl pyrazole-3-carboxylate, which crystallised from water in colourless prisms (0·9 g.), m. p. 141° (Found: C, 47·6; H, 4·7; N, 22·3. Calc. for $C_5H_6O_2N_2$: C, 47·6; H, 4·8; N, 22·2%). α-Chloroacrylic acid under identical conditions gave the same product, m. p. 141°.

(ii) α-Bromocrotonic acid (1 g.) treated similarly, gave methyl 4-methylpyrazole-3-carboxylate (0·51 g.), colourless prisms from water, m. p. 170° (Found: C, 51·2; H, 5·75; N, 19·8. Calc. for $C_6H_8O_2N_2$: C, 51·05; H, 5·7; N, 19·85%).

(iii) α-Bromo-ββ-dimethylacrylic acid (2 g.) was dissolved in excess of ethereal diazomethane and the solution kept at 20° for 12 days. Removal of solvent afforded a nitrogen-free product (1·8 g.), b. p. 98°/33 mm., which was identical with *methyl α-bromo-ββ-dimethylacrylate*, b. p. 76°/9 mm., $n_D^{21°}$ 1·4909 (Found: C, 37·8; H, 4·8. $C_6H_9O_2Br$ requires C, 37·3; H, 4·7%), prepared by esterification of the bromo-acid with methanol and sulphuric acid, since both specimens with aqueous ammonia (*d* 0·880) gave *α-bromo-ββ-dimethylacrylamide*, needles from light petroleum (b. p. 60—80°), m. p. and mixed m. p. 129° (Found: C, 34·0; H, 4·7; N, 7·5. C_5H_8ONBr requires C, 33·7; H, 4·5; N, 7·9%).

Reactions of Methyl α-Bromo-αβ-olefinic Esters with Methyl Diazoacetate.—(i) A solution of methyl α-bromoacrylate (1 g.) and methyl diazoacetate (2 g.) in light petroleum (b. p. 80—100°) (50 c.c.) was refluxed for 15 hours (during which the intensity of the deep yellow colour was much reduced) and then evaporated to dryness under reduced pressure. The solid residue of methyl pyrazole-3 : 5-dicarboxylate (1·3 g.) crystallised from water in colourless prisms, m. p. 152° (Found: N, 15·3. Calc. for $C_7H_8O_4N_2$: N, 15·2%). The same product (0·6 g.), m. p. 152°, was also obtained from methyl α-chloroacrylate (1 g.).

(ii) A solution of methyl α-bromocrotonate (1 g.) and methyl diazoacetate (1 g.) in light petroleum (b. p. 80—100°) (25 c.c.) after refluxing for 24 hours was still deeply coloured, in spite of the use of the excess of bromo-ester. Evaporation under reduced pressure gave a small residue of *methyl 4-methylpyrazole-3 : 5-dicarboxylate*, colourless prisms (0·15 g.) from water, m. p. 128—129° (Found: C, 48·85; H, 5·2; N, 14·0. $C_8H_{10}O_4N_2$ requires C, 48·5; H, 5·1; N, 14·1%), which was also obtained, in similar yield, from methyl α-chlorocrotonate under the same conditions.

(iii) A solution of methyl α-bromo-ββ-dimethylacrylate (1 g.) and methyl diazoacetate (1 g.) in light petroleum (b. p. 80—100°) (20 c.c.) was refluxed for 4 days, after which the solvent and diazo-ester were removed under reduced pressure. The residual nitrogen-free liquid, b. p. 70°/6 mm., was unchanged bromo-ester, identified by conversion into the amide, m. p. and mixed m. p. 128°.

Action of Diazomethane on Methyl α-Methoxyacrylate.—The methoxy-ester (1 g.) was treated with

excess of ethereal diazomethane at 20° for 4 days. Removal of solvent gave a liquid, b. p. *ca.* 135°, which by treatment with aqueous ammonia (*d* 0·880) was converted into 1-*methoxy*cyclo*propane*-1-*carboxyamide*; this crystallised from light petroleum (b. p. 40—60°) in colourless needles, m. p. 117°, which showed no unsaturation towards alkaline permanganate (Found: C, 52·2; H, 8·0; N, 11·9. $C_5H_9O_2N$ requires C, 52·2; H, 7·9; N, 12·2%).

Action of Methanolic Hydrogen Chloride on Methyl Methoxyacrylate.—The methoxy-ester (1 g.) was dissolved in methanol (5 c.c.) and saturated with dry hydrogen chloride at 0°. After ½ hour, the hydrogen chloride was removed by aeration and finally by neutralisation with barium carbonate. Evaporation of the solvent and extraction of the residue with ether gave methyl αα-dimethoxypropionate, b. p. 67°/20 mm., which on treatment with methanolic 2 : 4-dinitrophenylhydrazine sulphate gave the 2 : 4-dinitrophenylhydrazone of methyl pyruvate, m. p. 186—187°; it was also characterised by conversion, with aqueous ammonia, into αα-dimethoxypropionamide, m. p. 117° (Found: N, 10·5, Calc. for $C_5H_{11}O_3N$: N, 10·5%).

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