Baker : Synthesis of

# 97. Synthesis of Methyl $\alpha$ -Methoxyacrylate and $\alpha$ -Methoxyacrylonitrile: Characterisation of Methoxy-derivatives of Propionic Acid.

## By JOHN W. BAKER.

Satisfactory methods for the preparation of monomeric *a-methoxyacrylonitrile* and methyl *a*-methoxyacrylate have been worked out and, in the course of the investigation, a number of isomeric derivatives of methoxypropionic acids have been synthesised, characterised as their crystalline amides, and their constitutions established.

In the course of investigations which had as their aim the synthesis of derivatives of  $\alpha$ -alkoxyacrylic acids, various dimethoxy-, methoxyhydroxy-, and methoxyhalogeno-propionic esters have been prepared and their orientations established. All these esters are readily converted, by the action of cold aqueous ammonia, into highly crystalline amides, which are thus very convenient derivatives for the purpose of characterisation.

The initial line of attack was the action of sodium methoxide on halogenopropionic esters and this revealed points of interest regarding the relative reactivity of halogen substituents in the  $\alpha$ - and the  $\beta$ -position. The main product of the action of two molecular proportions of methyl-alcoholic sodium methoxide on methyl αβ-dichloropropionate is a liquid of relatively high boiling point which contains chlorine. Its structure has not yet been established, but it is certainly formed by the interaction of more than one molecule of the halogenoester. When only one molecular proportion of sodium methoxide is used, the overall result is the replacement of the  $\beta$ -chlorine atom to give methyl  $\alpha$ -chloro- $\beta$ -methoxypropionate, characterised as its amide (I), m. p. 61°. The same ester (identified as the amide) is obtained when one molecule of sodium methoxide acts upon methyl  $\alpha$ -chloro- $\beta$ -hydroxypropionate. If this ester is formed by a direct bimolecular replacement, the greater reactivity of the primary halide ( $\beta$ -) than of the secondary ( $\alpha$ -) is in harmony with the general conclusions from the recent work of Hughes, Ingold, and their collaborators (cf. inter alia, Hughes, Trans. Faraday Soc., 1941, 603). Treatment of  $\alpha\beta$ -dibromopropionic acid with two molecular proportions of sodium methoxide in dry alcohol, however, gives a highly unsaturated sodium salt (probably sodium  $\alpha$ -bromoacrylate) which, with a third molecule of sodium methoxide in the presence of a little quinol and subsequent acidification. affords a highly unsaturated acid, almost halogen-free. Esterification of this with dry methyl-alcoholic silver oxide and methyl iodide gives mainly methyl  $\alpha\beta$ -dimethoxypropionate (II), contaminated with a little unsaturated ester, since it is converted by ammonia into  $\alpha\beta$ -dimethoxypropionamide \* (III), m. p. 58°, identical with a specimen prepared by methylation of methyl  $\beta$ -hydroxy- $\alpha$ -methoxypropionate (below) and conversion of the product into the amide. The formation of the same chlorine-containing amide from both the  $\alpha\beta$ -dichloro- and the  $\alpha$ -chloro- $\beta$ -hydroxy-ester proves that (I) is the  $\alpha$ -chloro- $\beta$ -methoxy-derivative. Confirmation of this structure is derived from the observation that (I) is isomeric, but not identical, with  $\beta$ -chloro- $\alpha$ -methoxypropionamide (IV), m. p. 138°, which was synthesised in the following manner. Methyl methoxyacetate condenses with methyl formate in the presence of sodium to give the sodium derivative of methyl  $\alpha$ -methoxy- $\beta$ -hydroxyacrylate, which, after acidification, is reduced (without isolation) by hydrogen and a Raney-nickel catalyst (G.P. 524,086 of 1940) to methyl  $\alpha$ -methoxy- $\beta$ -hydroxypropionate, characterised as its *amide* (V), m. p. 71°. Treated with thionyl chloride and pyridine, this ester affords the corresponding  $\beta$ -chloro-ester, converted by aqueous ammonia into (IV).

The corresponding pair of methoxy-bromopropionamides has also been obtained. Methyl  $\alpha$ -bromo- $\beta$ -methoxypropionate, a specimen of which was kindly supplied by Dr. E. Rothstein of this University, is converted by ammonia into  $\alpha$ -bromo- $\beta$ -methoxypropionamide (VI), m. p. 84°. This is isomeric with  $\beta$ -bromo- $\alpha$ -methoxypropionamide (VII), m. p. 135°, which was obtained by a reaction sequence similar to that used by Price, Coynes, and De Los de Tar (J. Amer. Chem. Soc., 1941, 63, 2796) for the synthesis of  $\alpha$ -ethoxyacrylo-nitrile. This paper by the American authors was published just after the corresponding synthesis of  $\alpha$ -methoxy-acrylonitrile (VIII) had been achieved by the present author, using a similar route.  $\beta$ -Bromo- $\alpha$ -methoxy-

*propionitrile*, obtained in accordance with the scheme :  $CH_3 \cdot CHO + CH_3 \cdot OH + HCl \longrightarrow CH_3 \cdot CHCl \cdot O \cdot CH_3 \xrightarrow{Br_3} CHCl$ 

CH<sub>2</sub>Br·CHBr·O·CH<sub>3</sub>  $\xrightarrow{\text{CucN}}$  CH<sub>2</sub>Br·CH(O·CH<sub>3</sub>)·CN, is converted by dry hydrogen chloride and methyl alcohol in dry ether (cf. Houben and Pfankuch, *Ber.*, 1926, **59**, 2402) into the *imino-ether hydrochloride* (IX), CH<sub>2</sub>Br·CH(O·CH<sub>3</sub>)·C(O·CH<sub>3</sub>):NH,HCl, which readily loses methyl chloride when warmed to give the amide (VII). Decomposition of (IX) with ice affords *methyl*  $\beta$ -bromo- $\alpha$ -methoxypropionate (X).

Removal of hydrogen bromide from this ester occurs less readily than it does from the corresponding nitrile. Boiling pyridine, which readily converts the latter into the unsaturated nitrile (VIII), leaves a large proportion of the ester unchanged, but cold piperidine is effective, giving methyl  $\alpha$ -methoxyacrylate (XI). This ester was prepared in an impure condition by von Auwers (*Ber.*, 1911, 44, 3523) by the action of phosphoric oxide on methyl  $\alpha\alpha$ -dimethoxypropionate (XII), obtained by condensation of methyl pyruvate with methyl orthoformate, and now characterised as  $\alpha\alpha$ -dimethoxypropionamide (XIII), m. p. 117°. Prepared by either method, the unsaturated ester is converted by ammonia into  $\alpha$ -methoxyacrylamide (XIV), m. p. 109°. The same amide results from the elimination of hydrogen bromide from the bromo-methoxyamide (VII) by the action of methyl-alcoholic ammonia. Further confirmation that (VIII) is the  $\alpha$ -methoxy-compound accrues from the observation that it is converted, by the action of dry hydrogen chloride and methyl alcohol in dry

\* Methyl d-aβ-dimethoxypropionate and its amide were prepared by Frankland and Gebhard, J., 1905, 87, 864.

ether and decomposition of the imino-ether hydrochloride, into (XIII). The orientation of the addition of methyl alcohol thus parallels that of hydrogen bromide to the corresponding  $\alpha$ -ethoxyacrylonitrile (Price et al., loc. cit.) :

$$\underbrace{\operatorname{Me}}_{\delta-} \overset{\operatorname{H}}{\overset{}_{\delta+}} \underbrace{\operatorname{CH}}_{2} = \operatorname{C} \cdot \operatorname{C:N}_{0} \xrightarrow{\operatorname{HCl}} [\operatorname{CH}_{3} \cdot \operatorname{C}(\operatorname{O} \cdot \operatorname{CH}_{3})_{2} \cdot \operatorname{C}(\operatorname{O} \cdot \operatorname{CH}_{3})_{2} \cdot \operatorname{C}(\operatorname{O} \cdot \operatorname{CH}_{3})_{2} \cdot \operatorname{CO} \cdot \operatorname{NH}_{2} \xrightarrow{\operatorname{CO} \cdot \operatorname{NH}}_{2} \xrightarrow{\operatorname{CO} \cdot \operatorname{CH}_{3}}_{O_{\mathrm{C}}} \cdot \operatorname{CH}_{3} \cdot \operatorname{CBr}(\operatorname{OEt}) \cdot \operatorname{Ci}_{\mathrm{N}}^{\mathrm{C}} \xrightarrow{\operatorname{CO} \cdot \operatorname{CH}_{3}}_{O_{\mathrm{C}}} \cdot \operatorname{CO} \cdot \operatorname{CH}_{3} \cdot \operatorname{CBr}(\operatorname{OEt}) \cdot \operatorname{Ci}_{\mathrm{N}}^{\mathrm{C}} \xrightarrow{\operatorname{CO} \cdot \operatorname{NH}}_{2} \xrightarrow{\operatorname{CO} \cdot \operatorname{NH}}_{O_{\mathrm{C}}} \xrightarrow{\operatorname{CO} \cdot \operatorname{CH}}_{0} \xrightarrow{\operatorname{CO} \cdot \operatorname{CH}}_{O_{\mathrm{C}}} \cdot \operatorname{CI}_{\mathrm{C}} \xrightarrow{\operatorname{CO} \cdot \operatorname{CH}}_{0} \xrightarrow{\operatorname{CO} \cdot \operatorname{CO} \cdot \operatorname{CH}}_{0} \xrightarrow{\operatorname{CO} \cdot \operatorname{CO} \cdot \operatorname{CH}}_{0} \xrightarrow{CO} \xrightarrow{\operatorname{CO}$$

With either addendum the more reactive portion is the positive hydrogen, and the activating polarisation of the ethylenic bond resulting from the +T effect of the  $\alpha$ -alkoxy-group predominates over the deactivating polarisation which would result from the electron-attraction of the cyano-group.

 $\alpha$ -Methoxyacrylamide also readily adds on one molecule of bromine to give (probably)  $\alpha\beta$ -dibromo- $\alpha$ -methoxypropionamide, m. p. 106°, which is not very stable and, when warmed, readily loses hydrogen bromide.

### EXPERIMENTAL.

(All analyses are by Dr. G. Weiler of Oxford.)

Action of Sodium Methoxide on Methyl a $\beta$ -Dichloropropionate.—With 2 mols. One half of a solution of 4.6 g. of sodium in 100 c.c. of dry methyl alcohol was added dropwise with mechanical stirring to 15.7 g. of the chloro-ester and 0.1 g. of quinol at  $0^{\circ}$ . The remaining 50 c.c. was then added, and the mixture stirred at  $0^{\circ}$  for 2 hours and finally refluxed on a steam-bath for a further hour. After cooling, precipitated sodium chloride (9.5 g.) was removed by filtration, methyl alcohol distilled off through a column, and the product extracted with ether. The highly unsaturated yellow oil (4.5 g.) obtained by evaporation of the washed and dried ethereal solution gave a main fraction, b. p.  $140-145^{\circ}/9$  mm, of a colourless, unsaturated, viscous liquid which has not been identified (Found : C, 49.6; H, 6.35%).

With 1 mol. A solution of 2.3 g. of sodium in 50 c.c. of methyl alcohol was similarly added, during 2 hours, to 15.9 g. of the chloro-ester in 50 c.c. of ether at  $0^\circ$ ; the mixture was stirred for 14 hours at  $0^\circ$ , refluxed for 4 hour, kept at room temperature overnight, and worked up as before. Fractional distillation gave methyl a-chloro- $\beta$ -methoxypropionate, b. p. 65·5—66°/11 mm. (Found : C, 40·2; H, 6·4; Cl, 23·8. C<sub>5</sub>H<sub>9</sub>O<sub>3</sub>Cl requires C, 39·4; H, 5·9; Cl, 23·3%). The ester readily dissolved in aqueous ammonia (d 0.880) and evaporation of the solution afforded the corresponding *amide* (1), m. p. 61° after crystallisation from ether-ligroin (b. p. 40—60°) (Found : C, 35·3; H, 5·8; N, 10·1. C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>NCl

requires C, 34.9; H, 5.8; N, 10.2%). Action of Sodium Methoxide on Methyl a-Chloro-β-hydroxypropionate.—13.9 G. of this ester were similarly treated with 2.3 g. of sodium in 50 c.c. of dry methyl alcohol. After working up as before, distillation of the residue from the ethereal solution gave, in addition to a large amount of high-boiling residue, a fraction, b. p. 69°/14 mm., converted by aqueous ammonia ( $d \ 0.880$ ) into the amide (I), m. p. and mixed m. p. 61°.

Methyl  $\beta$ -Hydroxy-a-methoxypropionate.—A mixture of 23.2 g. of methyl methoxyacetate and 14 g. of methyl formate was added dropwise, with constant shaking, to 5.12 g. of "molecular" sodium under a little dry benzene, gently warmed on a steam-bath. An energetic reaction set in and, after 3 hours, the sodium had dissolved. The brown sticky mass of the sodium derivative of methyl  $\beta$ -hydroxy-a-methoxyacrylate was washed by decantation with cold dry ether and dissolved in the minimum quantity of cold water. The aqueous solution, acidified with 105 c.c. of 2N-sulphuric acid, was reduced with hydrogen at  $50^{\circ}/40$  atms. and a Raney nickel catalyst. After 6 days (cooling overnight) about 70% of the theoretical volume had been absorbed. The green solution was filtered and concentrated at  $30^{\circ}$  in a vacuum until oil separated. This was extracted with ethyl acetate and dried over sodium sulphate, and the solvent distilled off oil separated. This was extracted with ethyl acetate and dried over sodium sulphate, and the solvent distilled off through a Widmer column. Fractionation gave 8 g. of methyl  $\beta$ -hydroxy- $\alpha$ -methoxypropionate, b. p. 101–102°/15 mm. (Found : C, 44·5; H, 7·0. Calc. for  $C_{9}H_{10}O_{4}$ : C, 44·8; H, 7·5%), together with a fraction, b. p. 119–127°/16 mm., which gave a purple colour with ferric chloride. The ester was converted by aqueous ammonia into  $\beta$ -hydroxy- $\alpha$ -methoxypropionamide (V), m. p. 71° after crystallisation from acetone–ligroin (Found : C, 40·8; H, 7·6; N, 12·0.  $C_{4}H_{9}O_{3}N$  requires C, 40·3; H, 7·6; N, 11·8%). Attempts to dehydrate methyl  $\beta$ -hydroxy- $\alpha$ -methoxypropionate to methyl  $\alpha$ -methoxyacrylate with various reagents were unsuccessful, but distillation with phosphoric oxide under atmospheric pressure gave an ester, b. p. 128°/760 mm., which, since it gave a 2 : 4-dinitrophenylhydrazone, seems to be methyl pyruvate, formed by subsequent demethylation and ketonisation of the resulting methyl  $\alpha$ -hydroxyacrylate

and ketonisation of the resulting methyl a-hydroxyacrylate.

 $\beta$ -Chloro-a-methoxypropionamide (IV).—A solution of 2.7 g. of the corresponding hydroxy-ester in 3.5 g. of pyridine was treated with 2.4 g. of thionyl chloride. After initial self-heating, the mixture was warmed on a steam-bath until evolution of sulphur dioxide ceased. The product was extracted with ether and washed successively with saturated brine acidified with dilute hydrochloric acid, and water. Distillation of the residue from the dried ethereal solution gave a small quantity of a chlorine-containing ester, b. p. 88—90°/22 mm., rapidly converted by aqueous ammonia (d 0.880) into a crystalline mass of the amide. Recrystallisation from ether or methyl alcohol gave β-chloro-a-methoxy-propionamide (IV), m. p. 138° (Found : C, 35.3; H, 6.2; N, 9.8. C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>NCl requires C, 34.9; H, 5.9; N, 10.2%). Action of Sodium Methoxide on aβ-Dibromopropionic Acid.—The acid (23.2 g.) was added to a warm solution of 4.6 g. of sodium in 80 c.c. of dry methyl alcohol. Self-heating occurred and after ½ hour the mixture was nearly solid and more there are back and the proceeded. The proceeded was been back and the proceeded and the proceeded and the proceeded.

neutral. The separated white solid was highly unsaturated and was probably sodium a-bromoacrylate. The mixture was refluxed for 2 hours on a steam-bath and then 0.1 g. of quinol was added, followed by a solution of 2.3 g. of sodium in 50 c.c. of dry methyl alcohol. Refluxing was continued for 20 hours. The methyl alcohol was then distilled off, and the thick pasty mass washed with ether, covered with fresh ether, and just acidified (Congo-red) with dilute sulphuric acid. Rapid distillation of the residue from the washed and dried ethereal solution gave 4.5 g. of a fraction, b. p. 4 mm. A suspension of dry silver oxide in dry methyl alcohol was refluxed with 4 g. of this acid and methyl 132°/14 mm. 132'/14 mm. A suspension of dry silver oxide in dry methyl alcohol was refluxed with 4 g. of this acid and methyl iodide was added in small successive portions during 40 hours. After evaporation of the methyl alcohol the residue was extracted with dry ether and filtered from silver salts. Evaporation of the ethereal solution caused separation of a small amount of seemingly polymerised material, which was removed. Distillation of the residue gave *methyl* a $\beta$ -dimethoxypropionate (II), b. p. 74.5°/14 mm. (Found : C, 48.7; H, 8.0. C<sub>6</sub>H<sub>12</sub>O<sub>4</sub> requires C, 48.65; H, 8.1%). With concentrated aqueous ammonia it afforded a $\beta$ -dimethoxypropionamide (III), m. p. 58° after crystallisation from ether (Found : C, 45.4; H, 8.5; N, 9.9. C<sub>5</sub>H<sub>11</sub>O<sub>3</sub>N requires C, 45.1; H, 8.3; N, 10.5%). Methylation of 0.5 g. of methyl  $\beta$ -hydroxy-a-methoxypropionate by refluxing with 5 c.c. of methyl iodide and dry silver oxide gave a product converted by aqueous ammonia, in small yield, into the same amide, m. p. 53—56°, raised to 55—57° by admixture with (III), m. p. 58°.

β-Bromo-a-methoxypropionitrile and Methyl β-Bromo-a-methoxypropionate.—A mixture of 200 g. of paraldehyde and 220 g. of dry methyl alcohol was cooled in a freezing mixture and saturated with dry hydrogen chloride (250 g.). The top layer (325 g.) of methyl a-chloroethyl ether was dried with calcium chloride and used without further purification. 100 C.c. of dry bromine were added dropwise with constant shaking to 199 g. of the chloro-ether at 0°. After removal of dissolved hydrogen bromide by an air stream, distillation gave a main fraction (372 g.), b. p. 67—75°/21 mm., of methyl aβ-dibromoethyl ether, which was used without further purification. Redistillation gave a purer product, b. p. 67—69°/22 mm. with some loss. A solution of 196 g. of the dibromo-ether in 230 c.c. of sodium-dried ether was added to 90 g. of dry powdered cuprous cyanide in a large flask fitted with an efficient reflux condenser. The mixture was gently warmed, with constant shaking, until a brisk reaction, necessitating ice-cooling, had-subsided. The mixture was then refluxed for  $\frac{3}{4}$  hour and kept in the cold for 24 hours to allow separation of copper compounds. Ether from the filtrate and washings of the copper salts was distilled through a Widmer column. The dark coloured residual liquid was decanted from copper compounds which separated during concentration. Fractionation under reduced pressure gave a considerable fraction, b. p. 30—84°/15 mm., and then β-bromo-a-methoxypropionitrile (70 g.) was collected at 84—89°/16 mm. The pure nitrile, b. p. 54°/0·1 mm. or 94·5°/24 mm. (Found: C, 29·7; H, 3·9. C<sub>4</sub>H<sub>6</sub>ONBr requires C, 29·3; H, 3·7%), rapidly decomposed and was immediately converted either into the unsaturated nitrile or into the imino-ether hydrochloride. A mixture of 65 g. of the nitrile, 14 g. of dry methyl alcohol, and 350 c.c. of dry ether was asturated with dry hydrogen chloride at — 10° for 3—4 hours and then kept in a refrigerator for 18 hours. Thorough washing of the separated mass of crystals with dry ether is essen

ion analysis was carried out on an earlier sample which may have retained traces of free hydrogen chloride. The imino-ether hydrochloride, stirred under ether at 0°, was decomposed by gradual addition of melting ice. After complete solution had occurred, the stirring was continued at 0° for about 20 minutes to complete the decomposition (otherwise the product is contaminated with the amide) and the aqueous layer was extracted several times with ether. After removal of the solvent from the washed and dried extract through a Widmer column, fractionation of the residue gave 45 g. of methyl β-bromo-a-methoxypropionate (X), b. p. 49°/0.5 mm. (Found : C. 31.3; H, 4.8; Br, 40.2. C<sub>5</sub>H<sub>9</sub>O<sub>3</sub>Br requires C, 30.5; H, 4.6; Br, 40.6%).

requires C, 30.5; H, 406; Bf, 40.0%). The imino-ether hydrochloride readily decomposes on warming either alone or in aqueous solution to give  $\beta$ -bromo-amethoxypropionamide (VII), m. p. 135° after crystallisation from water (Found : C, 26.6; H, 4.5; N, 7.9; Br, 44.0. C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>NBr requires C, 26.4; H, 4.4; N, 7.7; Br, 44.0%). This amide is isomeric with a-bromo- $\beta$ -methoxypropionamide (VI), m. p. 84° after crystallisation from ether (Found : C, 26.6; H, 4.4%), which was prepared from a specimen of methyl a-bromo- $\beta$ -methoxypropionate kindly supplied by Dr. Rothstein of this University. a-Methoxyacrylonitrile (VIII).—Freshly distilled  $\beta$ -bromo-a-methoxypropionitrile (54 g.) was added dropwise to 50 g.

a-Methoxyacrylonitrile (VIII).—Freshly distilled  $\beta$ -bromo-a-methoxypropionitrile (54 g.) was added dropwise to 50 g. of boiling pyridine (dried over potassium hydroxide and distilled) under reflux, and boiling continued for 10 minutes thereafter. If the reactants are pure and dry, pyridine hydrobromide separates as a white crystalline mass from a red solution. After cooling, the pyridine hydrobromide was repeatedly extracted with boiling ether and the extracts were washed free from pyridine with 2N-hydrochloric acid and water. The ether was removed from the dried solution through a Widmer column, and the residue distilled. a-Methoxyacrylonitrile (VIII), b. p. 27.5°/15 mm. or 32.5°/23 mm., was obtained as a colourless mobile liquid (Found : C, 57.8; H, 6.5; N, 17.0. C<sub>4</sub>H<sub>5</sub>ON requires C, 57.8; H, 6.1; N, 16.9%). A solution of 1.c.c. of the unsaturated nitrile in 5 c.c. of dry ether and a few drops of dry methyl alcohol was saturated at 0° with dry hydrogen chloride. The solution (containing some crystalline material) was evaporated in a current

A solution of 1 c.c. of the unsaturated nitrile in 5 c.c. of dry ether and a few drops of dry methyl alcohol was saturated at 0° with dry hydrogen chloride. The solution (containing some crystalline material) was evaporated in a current of dry air under reduced pressure, and the yellow viscous mass extracted with warm dry ether. The residue from the ethereal solution crystallised after seeding. Crystallisation of the product from ether gave a saturated amide, m. p. 113°, depressed by admixture with a-methoxyacrylamide, m. p. 109°, but raised to 116° by admixture with  $\alpha$ -dimethoxypropionamide, m. p. 116° (below).

*Methyl a-Methoxyacrylate* (XI).—A solution of 18 g. of redistilled piperidine in its own volume of dry ether was added dropwise to a solution of 39 g. of methyl  $\beta$ -bromo-*a*-methoxypropionate and 0·1 g. of quinol in 50 c.c. of dry ether at 0°, more ether being added as the mixture became thick with separated piperidine hydrobromide. After keeping at room temperature for 18 hours, the piperidine hydrobromide was removed by filtration. The residue from the ethereal solution, freed from piperidine and solvent as above, was distilled. Methyl *a*-methoxyacrylate (18 g.), b. p. 51·5—52°/11 mm., was obtained (Found : C, 50·9; H, 7·2; OMe, 51·3.\* Calc. for C<sub>5</sub>H<sub>8</sub>O<sub>3</sub> : C, 51·7; H, 6·9; OMe, 53·4%). The ester was converted by ammonia into the same amide, m. p. and mixed m. p. 109°, as that prepared from the specime of ester obtained from methyl *aa*-dimethoxypropionate (XII). The latter ester, b. p. 59·5°/11 mm. (Found : C, 48·6; H, 8·2%), was obtained by the condensation of 18 g. of methyl pyruvate with 25 g. of methyl orthoformate in 90 c.c. of dry methyl alcohol containing 1 g. of ammonium chloride (von Auwers, *loc.* 45·8; H, 8·3; N, 10·95. C<sub>3</sub>H<sub>11</sub>O<sub>3</sub>N requires C, 45·1; H, 8·3; N, 10·5%). The unsaturated ester obtained by the action of phosphoric oxide on methyl *aa*-dimethoxypropionate by von Auwers's method had b. p. 55·5°/10 mm., but, in agreement with the findings of that author, did not seem to be quite pure (Found : C, 50·5; H, 8·0; OMe, 53·2%). It was probably contaminated with a little of the unchanged dimethoxypropionate by contaminated with a little of the unchanged is a *a-methoxyacrylamide* (XIV), m. p. 109° after crystallisation from ether (Found : C, 4<sup>4</sup>/<sub>8</sub>O<sub>3</sub> : C, 51·7; H, 6·9; OMe, 53·2%). It was probably contaminated with a little of the unchanged dimethoxypropionate by von Auwers's method had b. p. 55·5°/10 mm., but, in agreement with the findings of that author, did not seem to be quite pure (Found : C, 50·5; H, 8·0; OMe, 56·2.\* (Calc. for C<sub>3</sub>H<sub>8</sub>O<sub>3</sub> : C, 51·7; H, 6·9; OMe, 53·2%). It

a-Methoxyacrylamide (0.3 g.) was treated with 0.5 g. of dry bromine, both in solution in dry carbon tetrachloride, until just coloured and the solution was evaporated to dryness on a steam-bath. The product was dissolved in dry ether and concentrated, and light petroleum (b. p. 40-60°) added. The  $a\beta$ -dibromo-a-methoxypropionamide obtained had m. p. 106° after crystallisation from benzene-light petroleum (b. p. 60-80°). It readily lost hydrogen bromide in the air and was not quite pure (Found : Br, 60.2.  $C_4H_7O_2NBr_2$  requires Br, 61.3%).

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\* Unreliable values for methoxyl were obtained with all the compounds examined in this investigation, even when the purity of the compound was proved by the figures for carbon and hydrogen.