634. *Anodic Syntheses. Part V.* Electrolysis of N-Acylamino-acids. A Novel Alkoxylation Reaction.*

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Electrolysis of *N*-acyl-glycines and -DL-α-alanines in methanol gives *N*-methoxymethyl- and *N*-1′-methoxyethyl-amides respectively in good yields. Analogous reactions occur in both ethanol and *iso*propanol.

Under similar conditions *N*-acyl derivatives of 6-aminohexanoic acid, γ-aminobutyric acid, and β-alanine undergo the normal Kolbe reaction giving the corresponding derivatives of polymethylenediamines in *ca.* 20—40% yields.

The Kolbe synthesis of compounds of the type R·R by electrolysis of the acids $R{\cdot}CO_2H$ is known to be accompanied by side reactions, a number of which were described by Kolbe himself (*Annalen*, 1849, **69**, 257). The extent to which by-products are formed is governed both by the experimental conditions and, to a marked degree, by the structure of the acid electrolysed. A survey of the literature reveals that presence of substituents α to the carboxyl group has the most pronounced influence, as would be expected, and may result in the Kolbe coupling reaction being largely or completely suppressed. Thus although normal coupling occurs with alkyl hydrogen malonates (Brown and Walker, *ibid.*, 1891, **261**, 107; Hickling and Westwood, *J.*, 1938, 1039) and, to a smaller extent, with α-phenyl- (Fichter and Stenzl, *Helv. Chim. Acta*, 1939, **22**, 970) and α-aryloxy-acetic acids (*idem, loc. cit.*; Fichter and Kestenholz, *ibid.*, 1942, **25**, 785), and a few α-alkyl-acids, little or no coupling has been reported for most α-alkyl-acids, for α-methoxy-, α-hydroxy-, α-halogeno-, α-keto-, α-cyano-, and α-amino-acids (for a review see Brockman, "Electro-Organic Chemistry," New York, 1926) or for di- or tri-phenylacetic acid (van der Hoek and Nauta, *Rec. Trav. chim.*, 1942, **61**, 845; Riccoboni, *Gazzetta*, 1940, **70**, 748). However as the experimental conditions employed in much of the early work in this field cannot now be regarded as the most suitable for coupling, further study seemed desirable. Moreover an investigation of the competing reactions might well reveal new and valuable synthetic processes. With these considerations in mind an exploratory investigation of the electrolysis of a number of substituted acids has been put in hand. The results with *N*-acylamino-acids are reported in the present communication.

Fichter and Schmidt (*Helv. Chim. Acta*, 1920, **3**, 704) demonstrated that electrolysis, in aqueous solutions, of α-amino-acids or their *N*-acyl or *N*-sulphonyl derivatives led to complete disruption of the molecule and not to coupling of the Kolbe type. In the application of the Kolbe reaction to fatty acids the use of methanolic rather than aqueous solutions has frequently been found advantageous, and the present work has been confined to non-aqueous solutions. These have yielded results quite different from those reported by Fichter.

Electrolysis of *N*-benzoylglycine in methanol furnished in good yield (61%) a neutral product which, on the basis of the analytical results and the formation of bisbenzamidomethane (II) and formaldehyde on treatment with mineral acid, is formulated as *N*-methoxymethyl-benzamide (I; R = Ph). This structure was confirmed by treatment of *N*-hydroxymethyl-benzamide with methanolic hydrogen chloride (cf. U.S.P. 2,364,737; B.P. 557,932), which gave in 30% yield a product identical with that prepared anodically.

$$R{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H \longrightarrow R{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}OMe \quad (I) \qquad (Ph{\cdot}CO{\cdot}NH)_2CH_2 \quad (II)$$

$$R{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2H \longrightarrow R{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}OMe \quad (III)$$

Anodic methoxylation also took place readily with *N*-acetyl- and *N*-carbobenzyloxy-glycine, giving *N*-methoxymethyl-acetamide (I; R = Me) and -benzylurethane (I; R = $Ph{\cdot}CH_2{\cdot}O$) in 78 and 74% yield respectively. Similarly *N*-acetyl- and N-benzoyl-DL-α-alanine gave the *N*-1′-methoxyethyl-amides (III; R = Me and Ph) in 85 and 91% yield respectively.

The use of solvents other than methanol was also briefly investigated, and by electrolysis of *N*-benzoylglycine in ethanol and *iso*propanol, and of *N*-benzoyl-DL-α-alanine in ethanol, the corresponding ethoxy- and *iso*propoxy-alkylamides were obtained (56—70%).

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These reactions can be generalised as follows :

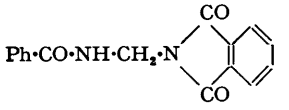
$$X\cdot NH\cdot CHR\cdot CO_2H + R'\cdot OH \longrightarrow X\cdot NH\cdot CHR\cdot OR' + CO_2$$

where X is acyl, R hydrogen or methyl, and R′ alkyl. The alkoxyalkyl-amides (acylamino-ethers) so produced are of a rare type hard to prepare in other ways. The yields are high and the products easily obtained as crystalline solids or colourless distillable liquids.

Electrolysis of *N*-phenylacetylglycine in acetic acid solution yielded *N*-(acetoxymethyl)-phenylacetamide (IV) (38%), previously prepared by the action of lead tetra-acetate on *N*-phenylacetylglycine (Süs, *Annalen*, 1949, **564**, 137).

From a few of the electrolyses in alcohols described above, small amounts (<15%) of α-diamine derivatives, the products of normal coupling, were also isolated.

$Ph\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot OAc$ (IV)



(V)

When *N*-methoxymethylbenzamide (I; R = Ph) and the corresponding ethoxy- and *iso*propoxy-compounds were heated with phthalimide, *N*-phthalimidomethylbenzamide (V) was obtained. A number of the other 1-alkoxyalkyl derivatives described above were also shown to react similarly with phthalimide and were conveniently characterised in this way.

The only previous well-authenticated example of anodic alkoxylation was reported by van der Hoek and Nauta (*loc. cit.*) who isolated methoxydiphenylmethane (35% yield) from the products formed by electrolysis of diphenylacetic acid in a mixture of methanol and pyridine. Anodic alkoxylations, in general, are reminiscent of the formation of alcohols on electrolysis of fatty acids in aqueous solution (Hofer and Moest, *Annalen*, 1902, **323**, 284). The Hofer–Moest reaction is promoted by various inorganic anions and can involve attack at positions both α and β to the eliminated carboxyl group (Kruis and Schanzer, *Z. physikal. Chem.*, 1942, **191**, *A*, 301). In the present work, however, no evidence was obtained of β-attack on derivatives of DL-α-alanine.

Several plausible mechanisms could be put forward to account for these anodic alkoxylations but it is not proposed to speculate on these at present. Experiments designed to provide information on this aspect are in hand. It is hoped to determine also the structural features which favour alkoxylation and related reactions.

After the study of derivatives of α-amino-acids, attention was directed to acids with the amino- and carboxyl groups separated from one another. Fichter and Schmidt (*loc. cit.*) were unable to detect the normal Kolbe reaction on electrolysis of β-alanine or its *N*-benzoyl derivative in aqueous solution, but, more recently, Offe (*Z. Naturforsch*, 1947, 2b, 182, 185) has stated that electrolysis in methanol of *N*-acyl or *N*-alkylsulphonyl derivatives of amino-acids other than those of the α-series leads to the corresponding derivatives of diamines by normal coupling. This conclusion was based on the results of electrolysing γ-phthalimido-butyric acid and derivatives of 6-aminohexanoic acid but yields were given in one case only. We find that normal Kolbe coupling occurs in the electrolysis in methanol of a considerable range of acylamino-acids other than those of the α-series. The reaction

$$X\cdot NH\cdot[CH_2]_n\cdot CO_2H \longrightarrow X\cdot NH\cdot[CH_2]_{2n}\cdot NH\cdot X$$

proceeds in about 30% yield where *n* is 2, 4, or 6. Thus 6-acetamido-, 6-benzamido-, and 6-carbobenzyloxyamino-hexanoic acids yielded the corresponding derivatives of 1 : 10-diamino-decane (31, 23, and 38% severally). 1 : 6-Biscarbobenzyloxyaminohexane was similarly prepared (35%) from γ-carbobenzyloxyaminobutyric acid. Electrolysis of *N*-benzoyl- and *N*-carbobenzyloxy-β-alanine furnished the derivatives of 1 : 4-diaminobutane in 20 and 33% yield. From *N*-benzoyl-β-alanine a small amount of 2-phenyloxazoline was isolated (in the form of its picrate) as by-product. In general, however, the nature of the side products in these reactions remains to be determined.

Experimental.

Apparatus.—Two cells, "A" and "B," were employed. These consisted of cylindrical glass vessels containing two parallel platinum plates, placed 1—2 mm. apart, as electrodes. In cell "A" the electrodes measured 4 × 2·5 cm., and in cell "B" 2·5 × 2·5 cm.

Electrolyses in Alcohols.—Technical absolute alcohols were used as solvents.

The acylamino-acid was dissolved in the alcohol to which sufficient sodium had previously been added to neutralise *ca.* 2% of the acid (except in the one experiment using *iso*propanol as solvent, in

which the ammonium salt was electrolysed). While the cell was cooled in an ice-bath, a current (*ca.* 0·1—0·2-amp./sq. cm. anode current density) was passed until the electrolyte became slightly alkaline. This process usually required *ca.* 3—6 times longer than the time calculated on the basis of the current and the amount of acid employed. At the end of the electrolyses, the cell contents were neutralised by the addition of a few drops of acetic acid and the products were isolated as described below.

N-*Methoxymethylbenzamide* (I; R = Ph).—(a) *Anodic synthesis.* *N*-Benzoylglycine (35·8 g.) in methanol (300 c.c.) was electrolysed in cell " A." After neutralisation of the cell contents the solvent was removed under reduced pressure and the residue crystallised from 1 : 5 light petroleum (b. p. 40—60°)–benzene and then from ether, giving N-*methoxymethylbenzamide* (20·0 g.) as prisms, m. p. 72·5° (Found: C, 65·7; H, 6·8; N, 8·3; OMe, 19·1. $C_9H_{11}O_2N$ requires C, 65·4; H, 6·7; N, 8·5; OMe, 18·8%). This, when heated with phthalimide, gave, in 70% yield, N-*phthalimidomethylbenzamide* (V), which crystallised from alcohol in needles, m. p. 184° (Found: C, 68·6; H, 4·4; N, 9·7. $C_{16}H_{12}O_3N_2$ requires C, 68·5; H, 4·3; N, 10·0%). This and the subsequent reactions with phthalimide were carried out by the following general method: The *N*-1′-alkoxyalkyl-amide and an equimolar quantity of phthalimide was heated rapidly to 180—220°, whereupon reaction commenced with evolution of vapours. The temperature of the mixture was raised during 5 minutes to 250°, evolution then ceasing. The mixture was then cooled and the resulting crude *N*-1′-phthalimidoalkyl-amide crystallised.

(b) A solution of anhydrous hydrogen chloride in methanol (1·37N.; 2·0 c.c.) was added to a warm (45°) solution of *N*-hydroxymethylbenzamide (18·0 g.) in anhydrous methanol (20 c.c.; dried over magnesium methoxide). The mixture was kept at 45—50° for ½ hour and then cooled to *ca.* −10° in ice-salt. The solid (12·5 g.), m. p. 40—60°, which separated was removed and extracted with water (100 c.c.) at 30°. The residue (8·1 g.), m. p. 69—70°, was recrystallised from 1 : 4 light petroleum (b. p. 40—60°)–ether and yielded *N*-methoxymethylbenzamide (6·0 g.) as prisms, m. p. 72° undepressed on admixture with a specimen from (a). The phthalimido-derivative had m. p. 184° undepressed on admixture with a specimen from (a).

Bisbenzamidomethane (II).—A mixture of *N*-methoxymethylbenzamide (1·0 g.) and hydrochloric acid (15% w/v; 20 c.c.) was heated rapidly (1 minute) to the b. p. Formaldehyde (identified as its 2 : 4-dinitrophenylhydrazone) was evolved, and on cooling of the acid solution a solid was deposited. This crystallised from ethanol, giving bisbenzamidomethane (0·6 g., 85%) m. p. 218° undepressed on admixture with an authentic specimen (Einhorn, *Annalen*, 1905, **343**, 226, gives m. p. 218°).

N-*Methoxymethylacetamide* (I; R = Me).—Acetylglycine (59 g.) in methanol (500 c.c.) was electrolysed in cell " A." Neutralisation and distillation of the cell contents gave the *amide* (40 g.) as a mobile oil, b. p. 90°/14 mm., n_D^{23} 1·4381, which was miscible with water (Found: C, 46·6; H, 9·0; N, 13·3. $C_4H_9O_2N$ requires C, 46·6; H, 8·8; N, 13·6%). The *phthalimido*-derivative, prepared in 46% yield, crystallised from alcohol in needles, m. p. 184° (Found: C, 60·3; H, 4·6; N, 12·6. $C_{11}H_{10}O_3N_2$ requires C, 60·5; H, 4·6; N, 12·8%).

Benzyl N-*Methoxymethylurethane* (I; R = $Ph{\cdot}CH_2{\cdot}O$) *and* 1 : 2-*Biscarbobenzyloxyaminoethane.*—*N*-Carbobenzyloxyglycine (10·5 g.) in methanol (20 c.c.) was electrolysed in cell " B." The cell contents were neutralised, the solvent was removed under reduced pressure, and the residue dissolved in light petroleum (b. p. 40—60°; 10 c.c.) containing a few drops of ethyl acetate. A solid (0·5 g.), m. p. 160°, separated and was recrystallised from the same solvent. This yielded 1 : 2-*biscarbobenzyloxyaminoethane*, m. p. 166·5° undepressed on admixture with a specimen prepared from benzyl chloroformate and ethylenediamine (Found: N, 8·5. $C_{18}H_{20}O_4N_2$ require N, 8·5%).

The mother-liquors were evaporated and the residue was distilled, giving *benzyl* N-*methoxymethylurethane* (6·0 g.), b. p. 70° (bath-temp.)/10^{-3} mm., n_D^{20} 1·5162 (Found: C, 61·7; H, 7·0; N, 6·9; OMe, 16·3. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7; N, 7·2; OMe, 15·9%). The *phthalimido*-derivative, prepared in 95% yield, crystallised from alcohol in needles, m. p. 121° (Found: C, 65·7; H, 4·5; N, 9·1. $C_{17}H_{14}O_4N_2$ requires C, 65·8; H, 4·5; N, 9·0%).

N-1′-*Methoxyethylacetamide* (III; R = Me).—Acetyl-DL-α-analine (13·1 g.) in methanol (60 c.c.) was electrolysed in cell " B." Neutralisation and distillation of the cell contents gave the *amide* (10·0 g.) as a water miscible oil, b. p. 71—73°/0·7 mm., n_D^{24} 1·4338 (Found: C, 51·3; H, 9·5; N, 12·2; OMe, 26·0. $C_5H_{11}O_2N$ requires C, 51·25; H, 9·5; N, 12·0; OMe, 26·5%).

N-1′-*Methoxyethylbenzamide* (III; R = Ph).—Benzoyl-DL-α-alanine (58 g.) in methanol (300 c.c.) was electrolysed in cell " A." The cell contents were neutralised, concentrated to *ca.* 75 c.c., and cooled. The solid (45 g.), m. p. 85°, which separated was removed. Evaporation of the mother-liquors and distillation of the residue gave a further quantity (7 g.) of product, b. p. 80° (bath-temp.)/10^{-4} mm., m. p. 80°. The crude products were combined and crystallised from ether, giving the *amide* (48 g.) as needles, m. p. 88·5° (Found: C, 66·9; H, 7·5; N, 7·7; OMe, 17·0. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3; N, 7·8; OMe, 17·3%). The *phthalimido*-derivative, prepared in 60% yield, crystallised from alcohol in needles, m. p. 199° (Found: C, 69·3; H, 4·9; N, 9·6. $C_{17}H_{14}O_3N_2$ requires C, 69·4; H, 4·8; N, 9·5%).

1 : 1-*Bisbenzamidoethane.*—A mixture of *N*-1′-methoxyethylbenzamide (5·0 g.) and 2N-hydrochloric acid (20 c.c.) was warmed rapidly (1 minute) to 80°. Acetaldehyde (identified as its 2 : 4-dinitrophenylhydrazone) was evolved, and on cooling of the acid solution a solid was deposited. This was crystallised from alcohol, giving 1 : 1-bisbenzamidoethane (3·0 g., 80%) as needles, m. p. 214° (Found: C, 71·3; H, 5·8; N, 10·3. Calc. for $C_{16}H_{16}O_2N_2$: C, 71·6; H, 6·0; N, 10·4%) (Kraut and Schwartz, *Annalen*, 1884, **223**, 40, give m. p. 202—204°).

N-*Ethoxymethylbenzamide and* 1 : 2-*Bisbenzamidoethane.*—*N*-Benzoylglycine (35·8 g.) in ethanol (300 c.c.) was electrolysed in cell " A." The cell contents were neutralised, filtered (charcoal), concentrated to *ca.* 100 c.c., and cooled, whereupon a solid (4·0 g.), m. p. 225—230°, separated. This was crystallised from glacial acetic acid, giving the diamide as needles, m. p. 244°, undepressed on admixture with an authentic specimen (Ladenburg, *Ber.*, 1895, 28, 3068, gives m. p. 244°).

The alcoholic mother-liquors were evaporated and the residue distilled, giving N-*ethoxymethylbenzamide* (20·0 g., 56%) as a viscous oil, b. p. 70—80° (bath-temp.)/10^{-3} mm., which slowly solidified. Low-temperature crystallisation from ether gave needles, m. p. 40° (Found: C, 67·2; H, 7·4; N, 7·8; OEt, 25·3. $C_{10}H_{13}O_2N$ requires C, 67·0; H, 7·3; N, 7·8; OEt, 25·1%). The phthalimido-derivative, prepared in 63% yield, had m. p. 186°, undepressed on admixture with the specimen prepared from *N*-methoxymethylbenzamide.

N-iso*Propoxymethylbenzamide and* 1 : 2-*Bisbenzamidoethane*.—A solution of *N*-benzoylglycine (3·58 g.) and the ammonium salt of *N*-benzoylglycine (from 3·58 g. of the acid) in *iso*propanol (100 c.c.) was electrolysed in cell " A." During the electrolysis a solution of *N*-benzoylglycine (28·6 g.) in *iso*propanol (200 c.c.) was added slowly (25 c.c./hour). The cell contents were neutralised and concentrated to 100 c.c., and then ether (100 c.c.) was added. The precipitated crude diamide (2·2 g.), m. p. 238°, was filtered off and the filtrate evaporated. Distillation of the residue gave N-iso*propoxymethylbenzamide* (27·5 g., 70%) as a viscous oil, b. p. 120° (bath-temp.)/5 × 10^{-3} mm., which slowly solidified and had f. p. 15° (Found: C, 68·6; H, 7·6; N, 7·6. $C_{11}H_{15}O_2N$ requires C, 68·4; H, 7·8; N, 7·3%). The phthalimido-derivative, prepared in 30% yield, had m. p. 185° undepressed on admixture with a specimen prepared from *N*-methoxymethylbenzamide.

N-1′-*Ethoxyethylbenzamide*.—Benzoyl-DL-α-alanine (6·6 g.) in ethanol (20 c.c.) was electrolysed in cell " B." Neutralisation and distillation of the cell contents gave the *amide* (5 g., 76%) as a viscous oil, b. p. 70—80° (bath-temp.)/10^{-4} mm., which slowly solidified. Crystallisation from ether at low temperature gave needles, m. p. 61·6° (Found: C, 68·7; H, 8·0; N, 7·5; OEt, 23·4. $C_{11}H_{16}O_2N$ requires C, 68·4; H, 7·8; N, 7·3; OEt, 23·3%).

N-(*Acetoxymethyl*)*phenylacetamide* (IV).—A solution of *N*-phenylacetylglycine (9·0 g.) and anhydrous sodium acetate (1·8 g.) in glacial acetic acid (60 g.) was electrolysed for 1 hour in cell " A," a current of 2·0 amps. being used. The cell contents were then evaporated under reduced pressure, the residue was dissolved in ether, and the solution washed with saturated aqueous sodium carbonate solution. On acidification of the aqueous extract, *N*-phenylacetylglycine (3·0 g.), m. p. 142°, was recovered. The ethereal solution was dried and evaporated. The residue on crystallisation from carbon tetrachloride and finally from alcohol gave *N*-(acetoxymethyl)phenylacetamide as needles (2·4 g.), m. p. 97·5° (Süs, *Annalen*, 1949, **564**, 137, give m. p. 98—99°) (Found: C, 64·1; H, 6·5; N, 6·9. Calc. for $C_{11}H_{13}O_3N$: C, 63·8; H, 6·3; N, 6·8%).

Bisphenylacetamidomethane.—A suspension of the preceding acetoxy-compound (2·1 g.) in hydrochloric acid (15% w/v; 20 c.c.) was gently boiled for 5 minutes. When the resulting solution was cooled, a solid separated. This on crystallisation from alcohol gave bisphenylacetamidomethane (0·5 g.), m. p. 209° (*idem*, *loc. cit.*, give m. p. 209—210°).

1 : 10-*Diacetamidodecane*.—6-Acetamidohexanoic acid (8·7 g.) in methanol (30 c.c.) was electrolysed in cell " B." The cell contents were neutralised, the solvent was evaporated, and the residue was crystallised (charcoal) from water, giving 1 : 10-diacetamidodecane (2·0 g.) as needles, m. p. 130° (Offe, *Z. Naturforsch*, 1947, **2** b, 185, gives m. p. 131° and 25—40% yield).

1 : 10-*Bisbenzamidodecane*.—6-Benzamidohexanoic acid (11·8 g.) in methanol (40 c.c.) was electrolysed in cell " B." The hot cell contents were neutralised, filtered (charcoal), and concentrated to 15 c.c., whereupon a solid (2·2 g.), m. p. 145°, separated. This was crystallised from 1 : 1 chloroform–ethyl acetate, giving 1 : 10-bisbenzamidodecane as needles, m. p. 152° (Found: C, 75·5; H, 8·5; N, 7·5. Calc. for $C_{24}H_{32}O_2N_2$: C, 75·7; H, 8·5; N, 7·4%) (*idem*, *loc. cit.*, gives m. p. 153°).

1 : 10-*Biscarbobenzyloxyaminodecane*.—6-Carbobenzyloxyaminohexanoic acid (13·3 g.), prepared in 80% yield from 6-aminohexanoic acid, had m. p. 55°. It was electrolysed in methanol (50 c.c.) in cell " B." The cell contents were extracted with boiling methanol, the extract was neutralised and filtered, and the filtrate concentrated to 20 c.c. Ether (100 c.c.) was added and the precipitated solid (4·2 g.), m. p. 115—120°, was crystallised from alcohol, giving 1 : 10-*biscarbobenzyloxyaminodecane* as needles, m. p. 123° (Found: C, 70·6; H, 8·3; N, 6·7. $C_{26}H_{36}O_2N_2$ requires C, 70·9; H, 8·2; N, 6·4%).

1 : 6-*Biscarbobenzyloxyaminohexane*.—γ-Carbobenzyloxyaminobutyric acid (11·0 g.), prepared in 68% yield from γ-aminobutyric acid, had m. p. 64·5°. It was electrolysed in methanol (100 c.c.) in cell " A." The hot cell contents were neutralised, filtered, and concentrated to 20 c.c., and ether (100 c.c.) was added. The solid (3·5 g.), m. p. 120°, which separated was crystallised from benzene giving 1 : 6-*biscarbobenzyloxyaminohexane* as needles, m. p. 126° (Found: C, 68·4; H, 7·3; N, 7·5. $C_{22}H_{28}O_4N_4$ requires C, 68·7; H, 7·4; N, 7·3%).

1 : 4-*Bisbenzamidobutane and* 2-*Phenyloxazoline*.—*N*-Benzoyl-β-alanine (17·4 g.) in methanol (55 c.c.) was electrolysed in cell " A," and the cell contents were then neutralised. The solvent was removed under reduced pressure, the residue dissolved in chloroform, and the solution washed with aqueous sodium carbonate, dried, and concentrated to 20 c.c. A solid (2·6 g.), m. p. 170°, which separated was crystallised from alcohol, giving 1 : 4-bisbenzamidobutane as needles, m. p. 176° undepressed on admixture with an authentic specimen (von Udránszky and Baumann, *Z. physiol. Chem.*, 1889, **13**, 174, give m. p. 175—176°).

The chloroform mother-liquors were evaporated. Distillation of the residue, which was accompanied by extensive decomposition, gave a heterogeneous oil (1·0 g.), b. p. 70°/3 × 10^{-3} mm. (Found: OMe, 7·6%). Treatment with an alcoholic solution of picric acid and crystallisation of the product from alcohol gave needles, m. p. 176—177° undepressed on admixture with the picrate of 2-phenyloxazoline (Gabriel and Heymann, *Ber.*, 1890, **23**, 2493, give m. p. 177°) (Found: N, 14·8. Calc. for $C_{15}H_{12}O_8N_4$: N, 14·9%).

1 : 4-*Biscarbobenzyloxyaminobutane*.—Carbobenzyloxy-β-alanine (15·6 g.) in methanol (50 c.c.) was electrolysed in cell " B." The cell contents were neutralised, diluted with chloroform, and filtered

(charcoal). The filtrate was concentrated to *ca.* 30 c.c., ether (50 c.c.) was added, and the precipitated solid (4·1 g.), m. p. 140°, separated. Crystallisation from cellosolve gave 1 : 4-*biscarbobenzyloxyamino-butane*, m. p. 150·5° (Found : C, 67·1; H, 6·9; N, 8·0. $C_{20}H_{24}O_4N_2$ requires C, 67·4; H, 6·8; N, 7·9%).

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