JOURNAL
OF
THE CHEMICAL SOCIETY.

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1. *The Conversion of Sucrose into Furan Compounds. Part II. Some 2 : 5-Disubstituted Tetrahydrofurans and their Products of Ring Scission.*

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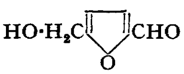
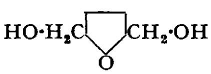
5-Hydroxymethylfurfuraldehyde is converted into 2 : 5-*bishydroxymethyltetrahydrofuran* and 5-hydroxymethylfuran-2-carboxylic acid into the corresponding tetrahydrofuran derivative by catalytic hydrogenation. Some derivatives of these compounds are described together with the products obtained by their ring fission. A new synthesis of adipic acid is recorded.

The preparation from sucrose of 5-hydroxymethylfurfuraldehyde has been described (J., 1944, 667) and it is envisaged that this compound might be an intermediate in the conversion of sucrose into useful compounds. We have now investigated the conversion of 5-hydroxymethylfurfuraldehyde into open-chain compounds. This may be accomplished in two ways: (i) by cleavage of the furan ring with hydrolytic agents, and (ii) by cleavage of the reduced furan ring. As examples of the first method may be considered the conversion of furfurylacrylic acid into 4-ketopimelic acid by treatment with ethyl-alcoholic hydrogen chloride (Marckwald, *Ber.*, 1887, **20**, 2811) and the conversion of δ-furfurylidenelævulic acid into 4 : 7-diketosebacic acid (Kehrer and Hofacker, *Annalen*, 1896, **294**, 165). An example of the second method is the cleavage of the tetrahydrofuran ring in 2 : 5-dimethyltetrahydrofuran by hydrogen halides (Freid and Kleene, *J. Amer. Chem. Soc.*, 1941, **63**, 2691) with the formation of 2 : 5-dihalogenohexanes. Ring fission of the tetrahydrofuran ring can also be brought about by acetyl chloride or acetic anhydride. Thus Paul obtained methyl 5-chloro-2-acetoxyvalerate from methyl tetrahydrofuran-2-carboxylate and acetyl chloride (*Compt. rend.*, 1941, **212**, 401) and 1 : 2 : 5-triacetoxypentane from acetoxymethyltetrahydrofuran and acetic anhydride in the presence of zinc chloride (*Bull. Soc. chim.*, 1941, **8**, 369). We have used method (ii) in the work described in this paper in obtaining open-chain compounds from 5-hydroxymethylfurfuraldehyde.

Relatively few 2 : 5-disubstituted derivatives of tetrahydrofuran have so far been described in the literature. Amongst these are 2 : 5-dimethyltetrahydrofuran obtained from the corresponding furan derivative by catalytic hydrogenation over palladised asbestos (Shuikin, Nikiforov, and Stolyarova, *J. Gen. Chem., U.S.S.R.*, 1937, **7**, 1501) and *cis*-tetrahydrofuran-2 : 5-dicarboxylic acid, which can be prepared, amongst other ways, by the action of alcoholic potassium hydroxide on *meso*-2 : 5-dibromoadipic acid. The preparation of this acid by the catalytic hydrogenation of furan-2 : 5-dicarboxylic acid (dehydromucic acid) has apparently not been described. On the other hand, many monosubstituted derivatives of tetrahydrofuran derived from the commercially available furfuraldehyde are known, *e.g.*, tetrahydrofuran-2-carboxylic acid and the corresponding 2-hydroxymethyl and 2-methyl derivatives.

5-Hydroxymethylfurfuraldehyde (I), readily prepared from sucrose (see J., 1944, 667), has been subjected to hydrogenation over Raney nickel and converted into 2 : 5-*bishydroxymethyltetrahydrofuran* (II) in excellent yield. This formed a liquid *bisacetoxy*-derivative and was characterised by the formation of a *bis*- 3 : 5-*dinitrobenzoate*.


(I.)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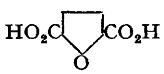
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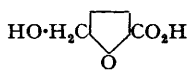
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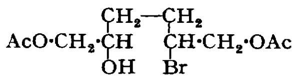
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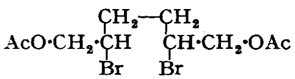
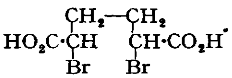
(V.)


$\mathrm{AcO{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2{-}CH_2{\cdot}CHBr{\cdot}CH_2{\cdot}OAc}$
(VI.)


$\mathrm{HO_2C{\cdot}CHBr{\cdot}CH_2{-}CH_2{\cdot}CHBr{\cdot}CO_2H}$
(VII.)

Unsuccessful attempts were made to oxidise it to the corresponding 2 : 5-dicarboxylic acid (III), degradation products only being formed. Thus oxidation with chromic anhydride led to complete degradation, and with nitric acid, succinic and oxalic acids were obtained.

Experiments on the ring fission of 2 : 5-bisacetoxymethyltetrahydrofuran were carried out and the following results obtained. On treatment at room temperature with a mixture of acetic anhydride, acetic acid and sulphuric acid, reagents used successfully in the acetolysis of benzylidene derivatives of the hexahydric alcohols (see, for example, Hann, Hudson, and Wolff, *J. Amer. Chem. Soc.*, 1942, **64**, 1493), the compound underwent ring fission to a small extent (10%) and crystalline 1 : 2 : 5 : 6-*tetra-acetoxyhexane* was isolated. Deacetylation by the Zemplén catalytic method gave crystalline 1 : 2 : 5 : 6-tetrahydroxyhexane (m. p. 98°), probably identical with one of the products (m. p. 95·5°) obtained by Wagner (*Ber.*, 1888, **21**, 3343) by the oxidation of diallyl with potassium permanganate. 2 : 5-Bisacetoxymethyltetrahydrofuran on treatment with hydrogen bromide in glacial acetic acid gave 2 : 5-*dibromo*-1 : 6-*diacetoxyhexane* (VI). 2-Bromo-5-hydroxy-1 : 6-diacetoxyhexane (V) is probably the first product of the reaction and in fact 2-*bromo*-1 : 5 : 6-*triacetoxyhexane* was produced as a by-product.

5-Hydroxymethylfurfuraldehyde can easily be converted into the corresponding carboxylic acid by oxidation with alkaline silver oxide (Reichstein, *Helv. Chim. Acta*, 1926, **9**, 1066). Hydrogenation of the carboxylic acid over Raney nickel led to the formation of a resinous material, probably a polymer of the polyester type, which, however, was readily broken down on treatment with ethyl-alcoholic hydrogen chloride; the product isolated was *ethyl 5-hydroxymethyltetrahydrofuran-2-carboxylate* and was characterised by the formation of a crystalline *amide*. The compound was better prepared by the hydrogenation of ethyl 5-hydroxymethylfuran-2-carboxylate. The free carboxylic acid was obtained by hydrolysis of the ethyl ester. The hydroxyl group in ethyl 5-hydroxymethyltetrahydrofuran-2-carboxylate was acetylated, and *ethyl 5-acetoxymethyltetrahydrofuran-2-carboxylate* isolated in good yield. *Ethyl 5-chloromethyltetrahydrofuran-2-carboxylate* was prepared from the corresponding hydroxy-compound by treatment with thionyl chloride and pyridine. Ring fission of ethyl 5-acetoxymethyltetrahydrofuran-2-carboxylate was effected by the use of the acetolysing reagent (acetic anhydride, acetic acid and sulphuric acid) and took place to a greater extent than in the case of 2 : 5-bisacetoxymethyltetrahydrofuran. Thus *ethyl* 2 : 5 : 6-*triacetoxyhexoate* was obtained in 55% of the theoretical yield.

5-Hydroxymethyltetrahydrofuran-2-carboxylic acid (IV) was oxidised with nitric acid, and *cis*-tetrahydrofuran-2 : 5-dicarboxylic acid (III) isolated in 60% yield. Attempts to prepare this dibasic acid by the catalytic hydrogenation of furan-2 : 5-dicarboxylic acid led only to poor yields of the desired product and the reduction was only accomplished by the use of high temperatures and pressures with Raney nickel as the catalyst. The catalytic hydrogenation of methyl furan-2 : 5-dicarboxylate was not accomplished.

The investigation of the ring fission of *cis*-tetrahydrofuran-2 : 5-dicarboxylic acid (III) led to a synthesis of adipic acid as below described. The dibasic acid was heated with hydrogen bromide in glacial acetic acid at 125° under pressure, and *meso*-2 : 5-dibromoadipic acid (VII) obtained in 60% yield. Catalytic hydrogenation of the latter over Raney nickel in the presence of calcium carbonate gave adipic acid in good yield. The series of reactions which constitute a synthesis of adipic acid from sucrose is as follows:

$$\begin{tikzcd}
\text{Sucrose} \arrow[r] & \begin{array}{c}\text{5-Hydroxymethyl-}\\\text{furfuraldehyde}\end{array} \arrow[r] & \begin{array}{c}\text{5-Hydroxymethyl-}\\\text{furan-2-carboxylic}\\\text{acid}\end{array} \arrow[r] & \begin{array}{c}\text{5-Hydroxymethyl-}\\\text{tetrahydrofuran-2-}\\\text{carboxylic acid}\end{array} \arrow[d] \\
& \text{Adipic acid} & \begin{array}{c}\textit{meso}\text{-2 : 5-Dibromo-}\\\text{adipic acid}\end{array} \arrow[l] & \begin{array}{c}\textit{cis}\text{-Tetrahydrofuran-}\\\text{2 : 5-dicarboxylic acid.}\end{array} \arrow[l]
\end{tikzcd}$$

Tetrahydrofuran-2 : 5-dicarboxylic acid proved to be a very stable compound. It was recovered unchanged after treatment with nitric acid at 95° and after treatment with fuming hydrochloric acid under pressure. The comparative stability of this ompound is further exemplified by the fact that *methyltetrahydrofuran-2 : 5-dicarboxylate*, obtained by boiling the corresponding dicarboxylic acid with methyl-alcoholic hydrogen chloride and characterised as its crystalline *diamide*, did not undergo ring cleavage on treatment with the acetolysing reagent.

EXPERIMENTAL.

2 : 5-*Bishydroxymethyltetrahydrofuran*.—5-Hydroxymethylfurfuraldehyde (10 g.), dissolved in ether (600 c.c.), was hydrogenated over Raney nickel at 130°/75 atms. for 6 hours. After filtration and evaporation of the filtrate the product, 2 : 5-*bishydroxymethyltetrahydrofuran*, distilled at 120° (bath temp.)/0·07 mm. as a fairly mobile, colourless liquid, $n_{\mathrm{D}}^{19^\circ}$ 1·4760. It was soluble in alcohol, acetone and water, slightly soluble in ether, and insoluble in light petroleum (Found: C, 54·7; H, 9·5. $C_6H_{12}O_3$ requires C, 54·6; H, 9·1%). A crystalline 3 : 5-*dinitrobenzoate* was obtained and had m. p. 173° (Found: C, 46·5; H, 3·4; N, 10·9. $C_{20}H_{16}O_{13}N_4$ requires C, 46·2; H, 3·1; N, 10·8%).

2 : 5-*Bisacetoxymethyltetrahydrofuran*.—2 : 5-Bishydroxymethyltetrahydrofuran (6 g.) was refluxed for 15 minutes with acetic anhydride (50 c.c.) and sodium acetate (6 g.), the product poured on ice, the acetic acid neutralised with sodium bicarbonate, and the solution extracted with chloroform. After the extract had been dried over anhydrous magnesium sulphate, it was evaporated to dryness, and a liquid obtained which distilled at 115° (bath temp.)/0·015 mm. The product was a colourless mobile liquid, $n_{\mathrm{D}}^{19^\circ}$ 1·4515. Yield, almost quantitative (Found: C, 55·5; H, 7·7. $C_{10}H_{16}O_5$ requires C, 55·5; H, 7·4%).

Acetolysis of 2 : 5-*Bisacetoxymethyltetrahydrofuran*.—The material (4·2 g.) was dissolved at 0° in the acetolysing reagent, prepared by mixing at 0° acetic anhydride (35 c.c.), acetic acid (15 c.c.), and concentrated sulphuric acid (1 c.c.) (see, for example, Hann, Hudson, and Wolff, *loc. cit.*), and was kept at room temperature for 24 hours. Thereafter it was poured on ice, neutralised with sodium bicarbonate, and extracted with ether. After the extract had been dried over anhydrous magnesium sulphate, it was evaporated to a syrup, which was distilled and collected in two fractions: Fraction 1 (2·6 g.), b. p. 140°/0·03 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4517; fraction 2 (1·2 g.), b. p. 170°/0·03 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4480. Both fractions were partly crystalline and after drying on porous tile the crystalline material in each was separately collected and recrystallised from ether–light petroleum. Each sample had m. p. 78°, either separately or in admixture. Yield, 0·21 g. (Found: C, 53·3; H, 6·6. $C_{14}H_{22}O_8$ requires C, 52·9; H, 6·9%). The material was 1 : 2 : 5 : 6-*tetra-acetoxyhexane*. Fraction 1 had *O*-acetyl, 42·4%, and fraction 2 had *O*-acetyl, 45·4%. The presence of only tetra-acetoxyhexane and bisacetoxymethyltetrahydrofuran being assumed, fraction 1 contains 0·26 g. of the former and fraction 2, 0·4 g. Thus the calculated yield of tetra-acetoxyhexane is 10·3% of the theoretical.

The crystalline tetra-acetoxyhexane was deacetylated by treatment with a trace of sodium in dry methyl-alcoholic solution in the usual way. A crystalline compound resulted, which, on being twice recrystallised from ethyl acetate–alcohol, had m. p. 98° and was 1 : 2 : 5 : 6-tetrahydroxyhexane. It was probably identical with one of the products of the action of potassium permanganate on diallyl (Wagner, *loc. cit.*) (Found : C, 48·5; H, 9·3. Calc. for $C_6H_{14}O_4$: C, 48·0; H, 9·3%).

Treatment of 2 : 5-*Bisacetoxymethyltetrahydrofuran with Hydrogen Bromide in Glacial Acetic Acid.*—The substance (4·4 g.) was dissolved in glacial acetic acid (4 c.c.), and the solution saturated at room temperature with dry hydrogen bromide, heated in a sealed tube at 125° for 2 hours, poured on ice, and extracted with ether. The extract was washed with sodium bicarbonate solution and with water, dried over anhydrous magnesium sulphate, and evaporated. A syrup (5 g.) was obtained which distilled in two fractions : Fraction 1, b. p. 105° (bath temp.)/0·008 mm., a very mobile, colourless liquid (1·2 g.), $n_{\mathrm{D}}^{23^\circ}$ 1·4806, was 2-*bromo*-1 : 5 : 6-*triacetoxyhexane* (Found : C, 42·7; H, 5·65; Ac, 36·8. $C_{12}H_{19}O_6Br$ requires C, 42·8; H, 5·6; Ac, 38·1%). Fraction 2, b. p. 145° (bath temp.)/0·08 mm., a fairly viscid, yellow liquid (3·8 g.), $n_{\mathrm{D}}^{22^\circ}$ 1·4957, was mainly 2 : 5-*dibromo*-1 : 6-*diacetoxyhexane* (Found : C, 33·2; H, 4·5; Ac, 26·8. $C_{10}H_{16}O_4Br_2$ requires C, 33·3; H, 4·4; Ac, 24·0%).

Oxidation of 2 : 5-*Bishydroxymethyltetrahydrofuran.*—A solution of the material (0·5 g.) in nitric acid (*d* 1·15) (30 c.c.) was slowly warmed to 100° and kept thereat for 1 hour, vigorous evolution of nitrous fumes occurring. The solution was diluted with water and evaporated at constant volume until most of the excess of nitric acid had disappeared. On evaporation to dryness a solid residue was left which after recrystallisation from ether gave (*a*) oxalic acid dihydrate (m. p. 101°) and (*b*) succinic acid (m. p. 186°).

Ethyl 5-*Hydroxymethyltetrahydrofuran*-2-*carboxylate.*—(*a*) 5-Hydroxymethylfuran-2-carboxylic acid (5 g.) was dissolved in water (500 c.c.) and hydrogenated over Raney nickel at 165°/60 atms. for 10 hours. On evaporation a red-brown resinous material remained, which was refluxed with ethyl alcohol (150 c.c.) containing 2% of hydrogen chloride for 7 hours. After neutralisation with silver carbonate, filtration and evaporation, a mobile liquid was obtained which distilled at 85° (bath temp.)/0·02 mm. and showed $n_{\mathrm{D}}^{17^\circ}$ 1·4540. Yield, 3·58 g. The distillate was a colourless mobile liquid, soluble in alcohol, ether, acetone and chloroform and slightly soluble in light petroleum.

(*b*) Ethyl 5-hydroxymethylfuran-2-carboxylate (35 g.) in ethyl acetate (600 c.c.) was hydrogenated over Raney nickel (1 g.) at 140°/130 atm. for 7 hours. Filtration of the resulting solution and evaporation of the solvent gave a mobile liquid, b. p. 85° (bath temp.)/0·02 mm., identical in properties with the material obtained in (*a*); this was *ethyl* 5-*hydroxymethyltetrahydrofuran*-2-*carboxylate*. Yield, 29 g. (Found : OEt, 25·3. $C_8H_{14}O_4$ requires OEt, 25·9%).

Ethyl 5-*Chloromethyltetrahydrofuran*-2-*carboxylate.*—Ethyl 5-hydroxymethyltetrahydrofuran-2-carboxylate (2 g.) was dissolved in dry pyridine (0·93 c.c.), and thionyl chloride (1·14 c.c.) carefully added at 0°. The mixture was heated at 100° for 1 hour, ether added, and the mixture washed successively with water, sodium bicarbonate solution, and water. After being dried over anhydrous magnesium sulphate, the ether was removed; the resulting liquid distilled at 82° (bath temp.)/0·023 mm. The product had $n_{\mathrm{D}}^{25^\circ}$ 1·4585 and was a colourless mobile oil. Yield, 0·75 g. The *chloromethyl* derivative was insoluble in water, very slightly soluble in light petroleum, and soluble in alcohol, ether, acetone, and chloroform (Found : C, 50·3; H, 6·5; OEt, 22·0. $C_8H_{13}O_3Cl$ requires C, 49·9; H, 6·7; OEt, 23·2%).

Ethyl 5-*Acetoxymethyltetrahydrofuran*-2-*carboxylate.*—The 5-hydroxymethyl ester (3 g.) was refluxed for 1 hour with acetic anhydride (10 c.c.) and fused sodium acetate (1·5 g.), and the solution poured into water and neutralised with sodium bicarbonate. The mixture was then extracted with ether, and the extract dried over anhydrous magnesium sulphate. Distillation of the solvent gave a liquid which distilled as a colourless mobile oil at 115° (bath temp.)/0·03 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4453. Yield, 80% of the theoretical (Found : Ac, 23·0. $C_{10}H_{16}O$ requires Ac, 20·0%).

5-*Hydroxymethyltetrahydrofuran*-2-*carboxyamide.*—A solution of the ethyl ester (0·2 g.) in ethyl alcohol (3 c.c.) was saturated with ammonia at 0°, kept at 0° for 24 hours, the solvent and ammonia then evaporated, and the residue recrystallised from acetone; m. p. 99°. Yield, 0·12 g. (Found : C, 49·7; H, 7·6; N, 10·3. $C_6H_{11}O_3N$ requires C, 49·7; H, 7·6; N, 9·7%).

5-*Hydroxymethyltetrahydrofuran*-2-*carboxylic Acid.*—The ethyl ester (6 g.) was heated at 70° with a slight excess of hydrated barium hydroxide (6·3 g.) for 1 hour, N-sulphuric acid added exactly to precipitate the barium as sulphate, which was removed by centrifuging, the supernatant liquid evaporated, and the residue extracted with chloroform. Evaporation of this extract gave a moderately viscid liquid which did not crystallise (Found : equiv., 150. $C_6H_{10}O_4$ requires equiv., 146).

Acetolysis of Ethyl 5-*Hydroxymethyltetrahydrofuran*-2-*carboxylate.*—The ester (0·5 g.) was added to a mixture of acetic anhydride (9 c.c.), acetic acid (4 c.c.), and concentrated sulphuric acid (0·25 c.c.) at 0°, the whole kept at room temperature for 40 hours and poured on ice, and the resulting solution extracted with chloroform. The extract was washed free from acid with dilute sodium bicarbonate solution, dried over anhydrous magnesium sulphate, and evaporated to dryness. The resulting syrup was distilled in two fractions : (*a*) Ethyl 5-acetoxymethyltetrahydrofuran-2-carboxylate (0·12 g.), b. p. 115° (bath temp.)/0·03 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4453 (Found : Ac, 21·8; OEt, 19·7. Calc. for $C_{10}H_{16}O_5$: Ac, 20·0; OEt, 20·8%). (*b*) *Ethyl* 2 : 5 : 6-*triacetoxyhexoate* (0·4 g.), b. p. 150° (bath temp.)/0·05 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4434 (Found : Ac, 36·7; OEt, 13·5. $C_{14}H_{22}O_8$ requires Ac, 38·1; OEt, 14·1%).

Oxidation of 5-*Hydroxymethyltetrahydrofuran*-2-*carboxylic Acid with Nitric Acid.*—The acid (5·5 g.) was dissolved in nitric acid (70 c.c., *d* 1·42) and heated at 80° until oxidation was complete. The solution, after dilution with water, was evaporated several times until the nitric acid had gone. The product was a crystalline solid, m. p. 126—127° after recrystallisation from ether–petrol and was *cis*-tetrahydrofuran-2 : 5-dicarboxylic acid (yield, 60% of the theoretical); the m. p. was not depressed by an authentic specimen prepared from *meso*-2 : 5-dibromoadipic acid by the method of Le Sueur and Haas (J., 1910, **97**, 173). The mother-liquors on evaporation gave a crystalline residue of indefinite m. p., probably a mixture of the *cis*- and the *trans*-isomer of the dicarboxylic acid.

Furan-2 : 5-*dicarboxylic Acid.*—Potassium hydrogen saccharate was boiled with 60% hydrobromic acid for 36 hours, and the required acid, m. p. 342°, isolated by Phelps and Hale's method (*J. Amer. Chem. Soc.*, 1901, **23**, 445). Yield, 56% of the theoretical. The substance was obtained in colourless plates after being treated with animal charcoal, but even the purest specimens reduced Fehling's solution.

Methyl Furan-2 : 5-*dicarboxylate.*—The dicarboxylic acid (20 g.) was boiled with 2% methyl-alcoholic hydrogen chloride for 6 hours. The main bulk of the ester crystallised on cooling and the remainder was obtained by neutralising the filtrate with silver carbonate, evaporating the solution, and recrystallising the residue from methyl alcohol. Yield, 90% of the theoretical, m. p. 110°.

Hydrogenation of Furan-2 : 5-*dicarboxylic Acid.*—The acid (10 g.), dissolved in 600 c.c. of water, was heated at 235° for 8 hours with Raney nickel (0·7 g.) at 135 atms. of hydrogen. On evaporation the solution gave a thick resinous mass, which appeared to be a polymer. The product was boiled for 5 hours with 2% methyl-alcoholic hydrogen chloride (100 c.c.), the acid neutralised with silver carbonate, and the solution filtered and evaporated. The residue was a mobile liquid (2·6 g.), b. p. 110—130°/0·04 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4505, which contained methyl tetrahydrofuran-2 : 5-dicarboxylate. A sample of the distillate (1 g.) was hydrolysed by heating with a solution of hydrated barium hydroxide (1·8 g.) for 2 hours at 80°. After exact neutralisation with N-sulphuric acid, removal of barium sulphate, and evaporation of the filtrate to dryness, the residue obtained was extracted with acetone, and the extract evaporated to give a crystalline residue from which *cis*-tetrahydrofuran-2 : 5-dicarboxylic acid, m. p. 126°, was obtained in small yield.

Methyl cis-*Tetrahydrofuran*-2 : 5-*dicarboxylate.*—The dicarboxylic acid (1 g.) was dissolved in 1% methyl-alcoholic hydrogen chloride and boiled for 5 hours. The acid was neutralised with silver carbonate, the solution filtered, and the filtrate evaporated to give a liquid (1·1 g.), b. p. 90° (bath temp.)/0·03 mm., $n_D^{15^\circ}$ 1·4550 (Found : OMe, 32·4. $C_8H_{12}O_5$ requires OMe, 33·0%).

cis-*Tetrahydrofuran*-2 : 5-*dicarboxyamide.*—A solution of the methyl ester (0·3 g.) in dry methyl alcohol (10 c.c.) was saturated with ammonia at 0° and kept overnight at this temperature, the solvent and ammonia then removed in a vacuum, and the residue recrystallised from acetone–methyl alcohol. Yield, 0·21 g., m. p. 189° (Found : C, 45·9; H, 6·0; N, 17·8. $C_6H_{10}O_3N_2$ requires C, 45·6; H, 6·3; N, 17·7%).

Attempted Acetolysis of Methyl Tetrahydrofuran-2 : 5-*dicarboxylate.*—The ester (0·8 g.) was dissolved in 20 c.c. of the acetolysing reagent (acetic anhydride 15 c.c., acetic acid 4·6 c.c., concentrated sulphuric acid 0·4 c.c.) at 0°, kept at room temperature for 10 days, and poured into ice-water; after being neutralised with sodium bicarbonate, the solution was extracted with chloroform. The extract on evaporation gave a liquid (0·6 g.), b. p. 90—100° (bath temp.)/0·03 mm., $n_D^{15^\circ}$ 1·4555 (Found : OMe, 32·5. Calc. for $C_8H_{12}O_5$: OMe, 33·0%), which was unchanged starting material.

Ring Fission of cis-*Tetrahydrofuran*-2 : 5-*dicarboxylic Acid with Hydrogen Bromide in Glacial Acetic Acid.*—The dicarboxylic acid (0·65 g.) was dissolved in glacial acetic acid (7 c.c.). A solution, saturated at 0°, of hydrogen bromide in glacial acetic acid (3·5 c.c.) was added, and the mixture heated in a sealed tube at 125° for 12 hours. The solution was poured into ice-water and extracted with ether, the extract dried (anhydrous magnesium sulphate), filtered, and evaporated, and the residue recrystallised from formic acid. The product was *meso*-2 : 5-dibromoadipic acid identical with the product obtained by Le Sueur and Haas (*loc. cit.*) by the bromination of adipyl chloride. Yield, 0·7 g., 60% of the theoretical, m. p. 192—194°.

Conversion of meso-2 : 5-*Dibromoadipic Acid into Adipic Acid.*—The dibromo-acid (2 g.) (m. p. 191°) was reduced with hydrogen over Raney nickel at 90 atms. for 4 hours at 125° in water in the presence of excess of calcium carbonate. The solution was filtered, evaporated to small bulk, acidified with dilute sulphuric acid, and extracted with ether. The extract, after being dried over magnesium sulphate, was distilled; the residue, on recrystallisation from nitric acid (*d*, 1·47), formed long needles (1 g.), m. p. 151—152°, not depressed by authentic adipic acid.

The authors are grateful to Imperial Chemical Industries Ltd., Dyestuffs Division, for financial assistance in aid of this work.

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