III.—*Glyoxaline*-4(5)-*formaldehyde.*

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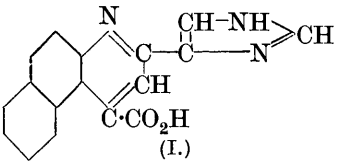
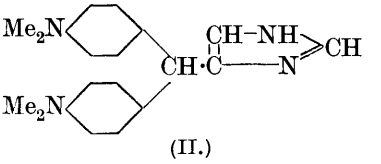
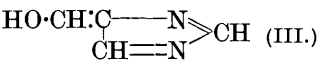
THIS research had the double object of studying the reactions of glyoxalinealdehydes, especially in comparison with benzaldehyde, and of determining the orienting effect of the carbonyl group in the methylation of these and related compounds. Glyoxaline-4(5)-formaldehyde had been shown previously to yield a cyanohydrin and a phenylhydrazone (Pyman, J., 1916, **109**, 186); the *anil*, *oxime*, *semicarbazone* and *sodium bisulphite compound* are now described. It had been condensed previously with malonic acid (Barger and Dakin, *Biochem. J.*, 1916, **10**, 376) and with hippuric acid, but attempts to convert it into glyoxaline-4(5)-acrylic acid by Perkin's method were unsuccessful (Pyman, *loc.*

cit.). Renewed attempts to effect its condensation with other compounds containing reactive methylene groups have been unsatisfactory; no condensation product was obtained with acetone, whilst condensation with acetophenone or ethyl acetate (by Claisen's method) gave very poor yields of the desired products. It condensed readily, however, with pyruvic acid and β-naphthylamine, yielding 2-[*glyoxalinyl*-4(5)]-β-*naphthacinchoninic acid* (I), and with dimethylaniline, yielding pp′-*tetramethyldiaminodiphenyl*[*glyoxalinyl*-4(5)-]*methane* (II), which gave a dye closely resembling malachite-green on oxidation.


(I.)


(II.)

Glyoxaline-4(5)-formaldehyde is not oxidised by air or ammoniacal silver nitrate. It does not undergo Cannizzaro's reaction, nor react with ammonia to give a compound of the hydrobenzamide type, being recovered unchanged in each case. It does not restore the colour to magenta decolorised by sulphurous acid, and does not undergo acetalisation by Fischer and Giebe's method (*Ber.*, 1897, **30**, 3053). Its aldehyde group does not react with magnesium methyl iodide. Attempts to convert it into a benzoin-like compound by means of potassium cyanide, and to condense it with nitromethane by means of alcoholic potassium hydroxide, resulted in uninviting resinous compounds.* In short, it does not show the properties typical of benzaldehyde which are shared by the aldehydes of many non-acidic heterocyclic compounds, such as furfuraldehyde, thiophen-α-aldehyde, and pyridine-α-aldehyde, but resembles the acidic *o*- and *p*-hydroxybenzaldehydes and pyrrole-α-aldehyde, which also fail to undergo many of the reactions characteristic of benzaldehyde (compare Pauly and von Buttlar, *Annalen*, 1911, **383**, 230). In common with these substances, its behaviour may be attributed either to the presence of an acidic group (·OH or :NH), or to stability in the tautomeric hydroxymethylene form,

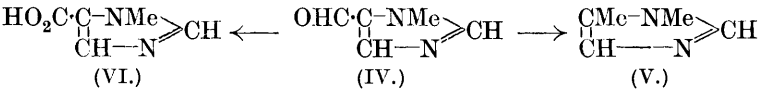

(III.)

which in this case is represented by the formula (III), and it was to be expected that its *N*-methyl derivatives would show the

* Details of these negative experiments are not recorded below, but will be found in the M.Sc. Tech. thesis of W. Hubball, University of Manchester, 1922.

typical reactions of benzaldehyde, just as anisaldehyde, for example, undergoes the Cannizzaro reaction, although *p*-hydroxybenzaldehyde fails to do so. For this reason and others the preparation of *N*-methylated glyoxalineformaldehydes was attempted by the methylation of glyoxalineformaldehyde, and 1-methylglyoxaline-5-formaldehyde was isolated but in so poor a yield that its properties could not be investigated fully. It proved, however, to undergo the Cannizzaro reaction normally, yielding the corresponding acid and alcohol (as did also 1 : 4-dimethylglyoxaline-5-formaldehyde, XIV).

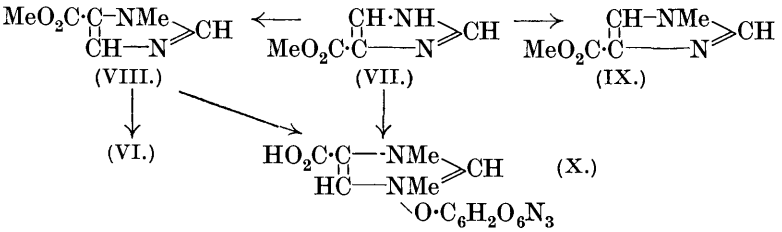
The methylation of glyoxalineformaldehyde was of interest also from another point of view. It has been shown previously (Hazeldine, Pyman, and Winchester, J., 1924, **125**, 1431; Balaban and Pyman, *ibid.*, p. 1564) that methylation of 4(5)-nitroglyoxaline and of 4(5)-bromoglyoxaline by methyl salts yields mainly 5-nitro-(or bromo)-1-methylglyoxaline with little 4-nitro(or bromo)-1-methylglyoxaline, and it was to be expected that the carbonyl group of glyoxaline-4(5)-formaldehyde would have a directive effect similar to that of the nitro-group, leading to the predominant formation of 1-methylglyoxaline-5-formaldehyde. Methylation of glyoxaline-4(5)-formaldehyde, however, proceeded very unsatisfactorily from the point of view of the formation of its monomethyl derivatives, for in several experiments under various conditions a considerable proportion was recovered unchanged, this indicating the formation of a corresponding quantity of the dimethylated quaternary salt. Consequently only poor yields of 1-*methylglyoxaline*-5-*formaldehyde* (IV) were obtained, and the isomeric 1-methylglyoxaline-4-formaldehyde was not isolated. The constitution of the base (IV) was proved through its reduction by hydriodic acid and phosphorus to 1 : 5-dimethylglyoxaline (V). On oxidation, it gave 1-*methylglyoxaline*-5-*carboxylic acid* (VI).



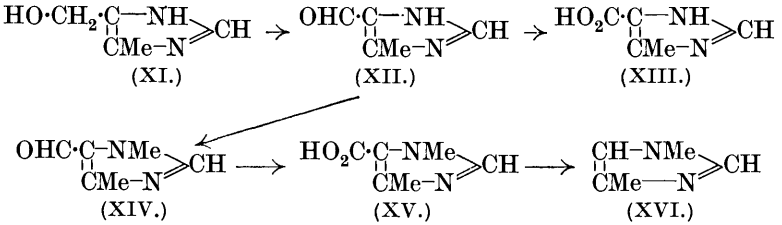
(VI.) (IV.) (V.)

The directive influence of the carbonyl group was studied further in the methylation of methyl glyoxaline-4(5)-carboxylate (VII) and 4(5)-methylglyoxaline-5(4)-formaldehyde. Methylation of the ester gave a fair yield (about 37%) of *methyl* 1-*methylglyoxaline*-5-*carboxylate* (VIII) together with a very small quantity (0·9%) of *methyl* 1-*methylglyoxaline*-4-*carboxylate* (IX), some unchanged material, and the dimethylated quaternary base isolated as 4(5)-*carboxy*-1 : 3-*dimethylglyoxalinium picrate* (X). The constitution of (VIII) was determined by hydrolysis, the acid (VI) being obtained, whilst the constitution of (X) was determined through its formation

by methylation and hydrolysis of (VIII), combined with the results of methoxyl and *N*-methyl determinations.



4(5)-*Methylglyoxaline*-5(4)-*formaldehyde* (XII) was prepared by the oxidation of 4(5)-methyl-5(4)-hydroxymethylglyoxaline (XI) by means of nitric acid; 4(5)-methylglyoxaline-5(4)-carboxylic acid (XIII), which had been prepared previously in other ways by Gerngross (*Ber.*, 1912, **45**, 509), was obtained as a by-product. The aldehyde has not been described previously, although Gerngross (*loc. cit.*) prepared its anil from 4(5)-methylglyoxaline-5(4)-glyoxylic acid.



Methylation of 4(5)-methylglyoxaline-5(4)-formaldehyde proceeded more smoothly than that of the lower homologue, and 1 : 4-*dimethylglyoxaline*-5-*formaldehyde* (XIV) was obtained in fair yield, but none of the isomeric 1 : 5-dimethyl-4-formaldehyde could be isolated. The constitution of (XIV) was determined (1) by oxidising it to the corresponding acid, 1 : 4-*dimethylglyoxaline*-5-*carboxylic acid* (XV), and decarboxylating this, 1 : 4-dimethylglyoxaline (XVI) being formed, and (2) through its formation by the oxidation of 1 : 4-dimethyl-5-hydroxymethylglyoxaline (Grindley and Pyman, J., 1927, 3128). The results of methylating glyoxaline-4(5)-formaldehyde, its 5(4)-methyl homologue, and methyl glyoxaline-4(5)-carboxylate show clearly that the carbonyl group, like the nitro-group and bromine atom, leads to the predominant formation of 5 : 1-methyl derivatives.

EXPERIMENTAL.

Glyoxaline-4(5)-formaldehyde has *M* 96 (by Rast's method) (Calc. for $C_4H_4ON_2$: *M*, 96). The *nitrate* crystallises from water

in colourless, elongated plates, m. p. 165° (corr.) (Found : C, 30·1; H, 3·2; N, 26·5. $C_4H_4ON_2,HNO_3$ requires C, 30·2; H, 3·1; N, 26·4%). The *hydrochloride* crystallises from water in colourless plates which are hygroscopic and after drying over sulphuric acid melt at 169—170° (corr.) (Found in dried salt : Cl, 26·6. $C_4H_4ON_2,HCl$ requires Cl, 26·8%).

Glyoxaline-4(5)-methylideneaniline.—The aldehyde (1 g.) dissolved in aniline (1·5 g.), but the clear liquid soon solidified. The *anil* crystallised from water in long, stout, colourless needles, m. p. 142—143° (corr.) (Found : C, 70·0; H, 5·5; N, 24·3. $C_{10}H_9N_3$ requires C, 70·2; H, 5·3; N, 24·6%). It is sparingly soluble in cold water, but readily soluble in alcohol or acetone.

Glyoxaline-4(5)-formaldoxime.—The aldehyde (0·5 g.), hydroxylamine hydrochloride (0·35 g.), and sodium carbonate (0·25 g.) gave on keeping in aqueous solution 0·53 g. of the *oxime*, m. p. 181—183°. After recrystallisation from alcohol, it formed colourless prisms, m. p. 183—184° (corr.) (Found : C, 43·0; H, 4·6; N, 37·7. $C_4H_5ON_3$ requires C, 43·2; H, 4·5; N, 37·8%). It is very sparingly soluble in cold water, alcohol, or acetone.

Glyoxaline-4(5)-formaldehyde semicarbazone, prepared from the aldehyde, semicarbazide hydrochloride, and sodium acetate in 75% yield, crystallised from water in colourless needles containing $1H_2O$, m. p. (after drying) 223—224° (corr.) (Found in air-dried substance : loss at 120°, 11·2. $C_5H_7ON_5,H_2O$ requires H_2O, 10·5%. Found in substance dried at 110° : C, 39·4; H, 4·4; N, 45·9. $C_5H_7ON_5$ requires C, 39·2; H, 4·6; N, 45·8%). It is fairly readily soluble in hot water, but sparingly soluble in cold water or hot alcohol.

The *glyoxaline-4(5)-formaldehyde-sodium bisulphite compound* crystallised from water in colourless plates, which darkened on heating to 200° (Found in air-dried material : Na, 11·1. $C_4H_5O_3N_2SNa$ requires Na, 11·5%). It is very readily soluble in hot water, moderately soluble in cold water, and almost insoluble in alcohol.

Glyoxaline-4(5)-formaldehyde and Acetone.—An attempt to condense the aldehyde with acetone under the conditions employed by Claisen (*Ber.*, 1881, **14**, 2468) for the condensation of benzaldehyde with acetone was unsuccessful. After a mixture of glyoxalineformaldehyde (0·3 g.), acetone (0·3 c.c.), and 10% aqueous potassium hydroxide (3 c.c.) had been kept for several days, the aldehyde was recovered in 64% yield.

Glyoxaline-4(5)-formaldehyde and Acetophenone.—Dry hydrogen chloride was passed through a solution of glyoxaline-4(5)-formaldehyde (1 g.) and acetophenone (1·26 g.) in glacial acetic acid for 3 hours. The solution was heated at 100°, kept over-night,

and mixed with aqueous sodium carbonate; an oil (0·6 g.) then separated. This was converted into picrate and crystallised fractionally; it then gave the picrate of the unchanged aldehyde (0·5 g.; yield, 14·8%), and a second picrate (0·07 g., m. p. 201° [corr.]; yield, 3·2%), which crystallised from water in yellow needles and gave fairly satisfactory analytical figures for glyoxaline-4(5)-methylideneacetophenone picrate (Found in air-dried salt: C, 51·2; H, 2·9; N, 16·6. $C_{12}H_{10}ON_2,C_6H_3O_7N_3$ requires C, 50·6; H, 3·0; N, 16·4%).

Glyoxaline-4(5)-formaldehyde and Ethyl Acetate.—In an attempt to condense these substances by Claisen's method (*Ber.*, 1890, **23**, 976), glyoxalineformaldehyde (1 g.), ethyl acetate (5 c.c.), and sodium (0·25 g.) were mixed and kept, first at the ordinary temperature and then on the water-bath. The product consisted of an ethyl acetate solution and a residue. The latter gave glyoxaline-formaldehyde picrate in 40% yield, whilst the substance dissolved in the ethyl acetate solution gave with picric acid a salt which, after repeated crystallisation from water, formed yellow needles, amounted to 0·15 g. (yield, 5%), blackened and decomposed at 250° after sintering from 230°, and gave figures on analysis indicating that it was the *picrate* of *ethyl urocanate* (ethyl glyoxaline-4(5)-acrylate) (Found: C, 42·4; H, 3·7. $C_8H_{10}O_2N_2,C_6H_3O_7N_3$ requires C, 42·5; H, 4·2%). Attempts to repeat the preparation of this compound were unsuccessful.

2-[*Glyoxalinyl*-4(5)]-β-*naphthacinchoninic Acid* (I).—The aldehyde (1 g.), pyruvic acid (1 g.), and β-naphthylamine (1·5 g.) were boiled in alcohol for 1 hour; the above acid (1·82 g.; yield, 62%) then separated. It crystallised from dilute acetic acid in very fine, yellow needles, decomp. 300° (Found: C, 70·5; H, 3·8; N, 14·6. $C_{17}H_{11}O_2N_3$ requires C, 70·6; H, 3·8; N, 14·5%). It is sparingly soluble in hot dilute acetic acid and almost insoluble in cold dilute acetic acid.

pp′-*Tetramethyldiaminodiphenyl*[*glyoxalinyl*-4(5)-]*methane* (II).—The aldehyde (1 g.), dimethylaniline (2·5 g.), and concentrated hydrochloric acid (2 g.) were heated for 4 hours at 100°. The viscous product was dissolved in water, basified with sodium carbonate, and distilled with steam to remove unchanged dimethylaniline. After cooling, the aqueous solution was decanted, and the amorphous product which had separated on the sides of the distillation flask was crystallised from alcohol. Yield, 1·73 g.; 52%. It was dissolved in alcohol and precipitated by ether; it then formed colourless clusters of needles, m. p. 190° (corr.), which soon became green in the air (Found: C, 74·9; H, 7·5; N, 17·6. $C_{20}H_{24}N_4$ requires C, 75·0; H, 7·5; N, 17·5%). The *leuco*-base

gave a clear, almost colourless solution in dilute hydrochloric acid.

Oxidation. The *leuco*-base (0·22 g.) was dissolved in water (100 c.c.) and very small quantities of hydrochloric and acetic acids, and lead dioxide paste (2 g.) was added gradually at 5° with constant shaking. After 5 minutes, sodium sulphate (0·25 g.) was added to the deep green solution, and lead sulphate was removed. The filtrate was mixed with ammonia; the colour base was then precipitated as a purple, crystalline powder (yield, 0·18 g.; 80%). It dissolves in acids to give deep green solutions, and dyes tanned cotton jade-green.

Methylation of Glyoxaline-4(5)-formaldehyde.—When glyoxaline-formaldehyde (1 g.) and methyl sulphate (1 c.c.) were mixed and warmed gently, a vigorous reaction took place. The product was dissolved in water, basified with sodium carbonate, and extracted with ether, crude 1-methylglyoxaline-5-formaldehyde (0·1 g.) being thus removed. It was converted into picrate and gave after crystallisation 0·2 g. of the pure salt (yield, 5·7%). From the alkaline mother-liquor glyoxalineformaldehyde was recovered as picrate in 44% yield.

Methylation of glyoxalineformaldehyde with either methyl iodide or methyl sulphate and sodium hydroxide gave none of the required product.

1-*Methylglyoxaline-5-formaldehyde picrate* crystallises from water in yellow, elongated plates, m. p. 170° (corr.) (Found: C, 39·1; H, 2·7; N, 20·7. $C_5H_6ON_2,C_6H_3O_7N_3$ requires C, 38·9; H, 2·6; N, 20·7%). The corresponding base (IV) crystallised from alcohol in colourless prisms, but the quantity available was insufficient for its complete purification by reason of its hygroscopic character. It was very readily soluble in water, alcohol, ether, or chloroform.

The *nitrate* crystallises from water in colourless prisms, m. p. 175° (corr.; eff.). Its aqueous solution reacts acid to litmus [Found in salt dried at 100° (loss 2·2%): C, 34·4; H, 4·2. $C_5H_6ON_2,HNO_3$ requires C, 34·6; H, 4·1%].

Reduction. 1-Methylglyoxaline-5-aldehyde (0·34 g.), red phosphorus (0·004 g.), and hydriodic acid (2 c.c.) were heated for 6 hours at 160°. The product was mixed with water and extracted with chloroform, then the aqueous solution was saturated with potassium carbonate and again extracted with chloroform. This left an oil which was converted into picrate, and after recrystallisation from water 1 : 5-dimethylglyoxaline picrate (0·38 g.; yield, 38%; m. p. 168—169°) was obtained. It did not depress the m. p. of a known specimen of 1 : 5-dimethylglyoxaline picrate, but its mixtures with

1 : 4-dimethylglyoxaline picrate (m. p. 167—168°) and 1-methylglyoxaline-5-formaldehyde picrate (m. p. 170°) were depressed to 136—142° and 145—150°, respectively.

Oxidation. To 1-methylglyoxaline-5-aldehyde (0·48 g.) in water (5 c.c.), potassium permanganate (0·44 g.) and sulphuric acid (0·4 c.c.) in water (20 c.c.) were added. After 4 hours, the mixture was heated for ½ hour at 100°, then basified with sodium carbonate, filtered from inorganic matter, and extracted with chloroform. This took up unchanged aldehyde, which was recovered as picrate in 16% yield. The aqueous mother-liquor was rendered faintly acid and evaporated to dryness, and the residue was extracted with absolute alcohol. The extracted substance was mixed with alcoholic picric acid; *5-carboxy-1-methylglyoxaline picrate* then separated in 14% yield (0·24 g.; m. p. 197—198°). This salt crystallises from water in large, anhydrous, irregular leaflets, m. p. 198—199° (corr.; eff.). It is sparingly soluble in cold water or alcohol, but readily soluble in hot water (Found: C, 37·5; H, 2·5; N, 19·6.

$$C_5H_6O_2N_2,C_6H_3O_7N_3$$

requires C, 37·2; H, 2·5; N, 19·7%).

Action of potassium hydroxide. 1-Methylglyoxaline-5-formaldehyde (0·24 g.) was dissolved by warming with 50% aqueous potassium hydroxide (3 c.c.). The solution was kept for 24 hours, acidified faintly with hydrochloric acid, and evaporated to dryness. The residue was extracted with absolute alcohol, and picric acid added; *1-methyl-5-hydroxymethylglyoxaline picrate* (0·28 g.; m. p. 166°; yield, 37·5%) then separated first, followed by 5-carboxy-1-methylglyoxaline picrate (0·23 g.; m. p. 192—196°; yield, 30%). The latter did not depress the m. p. of an authentic specimen.

1-Methyl-5-hydroxymethylglyoxaline picrate crystallised from water in yellow prisms, m. p. 166° (corr.). It is sparingly soluble in cold water [Found in salt dried at 100° (loss 0·6%): C, 38·9; H, 3·3. $C_5H_8ON_2,C_6H_3O_7N_3$ requires C, 38·7; H, 3·2%].

4(5)-Methylglyoxaline-5(4)-formaldehyde (XII).—5(4)-Methyl-4(5)-hydroxymethylglyoxaline (8 g.) was oxidised by heating on the water-bath with nitric acid (12 c.c.; *d* 1·42), and the product was worked up as in the oxidation of the lower homologue (Pyman, J., 1916, **109**, 188); 4(5)-methylglyoxaline-5(4)-formaldehyde (4·5 g., crude; m. p. 150—160°; yield, 57%) and 4(5)-methylglyoxaline-5(4)-carboxylic acid (1·3 g., crude; m. p. 202°; yield, 14·4%) were then obtained. After recrystallisation from water, the acid formed clusters of long needles, m. p. 222—223° with effervescence. Gerngross (*loc. cit.*) gives m. p. 223°.

4(5)-Methylglyoxaline-5(4)-formaldehyde crystallises from water in anhydrous, colourless, elongated prisms, m. p. 167° (corr.). It is

sparingly soluble in cold water, but readily soluble in alcohol (Found: C, 54·8; H, 5·6. $C_5H_6ON_2$ requires C, 54·6; H, 5·5%). The *picrate* crystallises from water in anhydrous, yellow needles, m. p. 180—181° (corr.) (Found: C, 38·6; H, 2·8; N, 21·1. $C_5H_6ON_2,C_6H_3O_7N_3$ requires C, 38·9; H, 2·7; N, 20·7%). The anil, prepared from this aldehyde in the usual way, crystallised from alcohol in colourless plates, m. p. 224° (corr.) (Found: C, 71·2; H, 6·1. Calc.: C, 71·4; H, 5·9%). Gerngross (*loc. cit.*), who prepared this anil from 4(5)-methylglyoxaline-5(4)-glyoxylic acid, gives m. p. 224°.

Preparation of 1 : 4-*Dimethylglyoxaline*-5-*formaldehyde* (XIV).—(A) *By methylation of* 4(5)-*methylglyoxaline*-5(4)-*formaldehyde.* 4(5)-Methylglyoxaline-5(4)-formaldehyde (9·4 g.) and methyl sulphate (9·4 c.c.) were heated at 100° for 20 minutes. The product was mixed with aqueous sodium carbonate, and extracted with chloroform, which collected 5·24 g. of colourless needles, m. p. (crude) 50—70°. This was added to picric acid (12 g.) in methyl alcohol; 11·0 g. of pure 1 : 4-dimethylglyoxaline-5-formaldehyde picrate (yield, 36%) were then obtained. The aqueous alkaline liquor was neutralised with hydrochloric acid and evaporated to dryness, and the residue extracted with alcohol, which removed crude unmethylated aldehyde. This was purified as picrate, 5·1 g. (17% unchanged) being obtained.

(B) *By oxidation of* 1 : 4-*dimethyl*-5-*hydroxymethylglyoxaline.* 1 : 4-Dimethyl-5-hydroxymethylglyoxaline (2·77 g.) was oxidised with concentrated nitric acid (3 c.c.), and the product worked up for the aldehyde in the usual way; 2·5 g. (yield, 92%), m. p. 60—70°, were obtained.

1 : 4-*Dimethylglyoxaline*-5-*formaldehyde* crystallises from water in colourless, elongated prisms, containing $1H_2O$, which melt at 70° (corr.) after drying in a vacuum (Found: loss, 13·4. $C_6H_8ON_2,H_2O$ requires H_2O, 12·7%. Found in dried substance: C, 57·9; H, 6·3; N, 22·6. $C_6H_8ON_2$ requires C, 58·1; H, 6·5; N, 22·6%). It is very readily soluble in water, alcohol, or chloroform, and slightly soluble in ether. The *picrate* crystallises from water in small, yellow, anhydrous needles, m. p. 212—213° (corr.). It is almost insoluble in cold water, alcohol, or acetone (Found: C, 40·9; H, 3·2; N, 19·8. $C_6H_8ON_2,C_6H_3O_7N_3$ requires C, 40·8; H, 3·1; N, 19·8%).

Oxidation. 1 : 4-Dimethylglyoxaline-5-formaldehyde is very resistant to oxidation. It was recovered to the extent of 85% unchanged after heating with 10 parts of concentrated nitric acid for 5 hours at 120°, but could be oxidised to the carboxylic acid by means of acid permanganate. The aldehyde (0·8 g.) in water

(25 c.c.) was cooled with ice, and a solution of potassium permanganate (0·6 g.) and sulphuric acid (0·4 c.c. conc.) in water (50 c.c.) was added in the course of 2 hours. The solution was filtered, concentrated to small bulk, mixed with sodium carbonate, filtered from manganese carbonate, made faintly acid to methyl-orange with hydrochloric acid, and extracted with ether and chloroform, which removed unchanged aldehyde (0·33 g.; yield, 41%). The aqueous solution was evaporated to dryness under diminished pressure, and the residue extracted with absolute alcohol. The extract gave on evaporation a colourless solid (0·54 g.), which was converted into the picrate, and this crystallised from water, 1·08 g. of pure 5-carboxy-1 : 4-dimethylglyoxaline picrate being obtained; yield, 45%.

1 : 4-*Dimethylglyoxaline-5-carboxylic acid* crystallises from water in colourless, anhydrous needles, m. p. 205—206° (corr.; eff.) (Found: C, 51·3; H, 5·7. $C_6H_8O_2N_2$ requires C, 51·4; H, 5·7%). It is readily soluble in water or alcohol, but insoluble in ether or acetone. The *picrate* crystallises from water in small, yellow needles containing $1H_2O$ and after drying at 100° has m. p. 186—187° (corr.) (Found in air-dried salt: loss at 100°, 4·6.

$$C_6H_8O_2N_2,C_6H_3O_7N_3,H_2O$$

requires H_2O, 4·6%. Found in dried salt: C, 39·3; H, 3·0. $C_6H_8O_2N_2,C_6H_3O_7N_3$ requires C, 39·0; H, 3·0%).

Decarboxylation. When the acid (0·14 g.) was heated above its m. p., it effervesced and an oil distilled. The distillate and residue were combined, and converted into picrate. After crystallisation from water, 0·11 g. of a picrate (yield, 34%), m. p. 166—167°, was obtained, and identified as 1 : 4-dimethylglyoxaline picrate (m. p. 167—168°), since it did not depress the m. p. of this salt in admixture with it. A mixture of this picrate with 1 : 5-dimethylglyoxaline picrate (m. p. 168—169°) melted at 133—135°, and a mixture with 5-carboxy-1 : 4-dimethylglyoxaline picrate melted at 146—148°.

Action of potassium hydroxide. 1 : 4-Dimethylglyoxaline-5-formaldehyde (0·65 g.) was dissolved in a solution of potassium hydroxide (5·0 g.) in water (10 c.c.), and the mixture kept for 24 hours. The product was acidified faintly with hydrochloric acid and evaporated to dryness, and the residue extracted with absolute alcohol. Picric acid was added to the extract, and the picrates were crystallised fractionally; 1 : 4-dimethyl-5-hydroxymethylglyoxaline picrate (0·84 g.; m. p. 166—167°, alone or mixed with a known specimen; yield, 45%) and 5-carboxy-1 : 4-dimethylglyoxaline picrate (0·21 g.; m. p. 203—204°, alone or mixed with a known specimen; yield, 14%) were then obtained.

Methylation of Methyl Glyoxaline-4(5)-*carboxylate*.—Methyl glyoxaline-4(5)-carboxylate (4·5 g.) and methyl sulphate (4·5 c.c.) were mixed and warmed gently. After the vigorous reaction had subsided, the mixture was heated for ½ hour at 100°, then basified with sodium carbonate, and extracted with chloroform. The chloroform on evaporation left an oil (3·1 g.), which was converted into picrate, and this crystallised from methyl alcohol; 5-carbomethoxy-1-methylglyoxaline picrate (4·38 g.; m. p. 169°; yield, 32·6%) and 4(5)-carbomethoxyglyoxaline picrate (0·47 g.; yield, 3·7%) were then isolated. The aqueous mother-liquor was neutralised with hydrochloric acid, and evaporated to dryness under diminished pressure. The residue was extracted with absolute alcohol and the extracted material was converted into picrate and recrystallised from water; 4(5)-carboxy-1 : 3-dimethylglyoxalinium picrate (1·72 g., m. p. 216—217°; yield, 13·1%) was then obtained. In a subsequent experiment in which 9 g. of ester were methylated, rather better yields were obtained, namely, 37% of 5-carbomethoxy-1-methylglyoxaline picrate, 26% of the picrate of the unchanged ester, and 16% of the 4(5)-carboxy-1 : 3-dimethylglyoxalinium picrate; in addition a very small quantity of picrate (0·24 g.; m. p. 171—172° [corr.]; yield, 0·9%) was isolated which was doubtless *methyl* 1-*methylglyoxaline*-4-*carboxylate*, judging from the results of analysis and the fact that it depressed the m. p. of the other products of the reaction (Found : C, 39·2; H, 3·0. $C_6H_8O_2N_2$,$C_6H_3O_7N_3$ requires C, 39·0; H, 3·0%). This substance crystallised from water in yellow prisms, m. p. 171—172° (corr.), which were sparingly soluble in cold water or alcohol.

Methyl 1-*methylglyoxaline*-5-*carboxylate* crystallises from absolute methyl alcohol in colourless, elongated prisms, m. p. 68—70° (corr.) (Found : C, 51·3; H, 5·8; N, 20·2. $C_6H_8O_2N_2$ requires C, 51·4; H, 5·7; N, 20·0%). It is soluble in water, alcohol, or chloroform, but sparingly soluble in cold ether.

The *picrate* crystallises from water in small, yellow, anhydrous prisms, m. p. 171° (corr.) (Found : C, 39·3; H, 3·2; N, 18·7; OMe, 9·1; NMe, 7·6. $C_6H_8O_2N_2$,$C_6H_3O_7N_3$ requires C, 39·0; H, 3·0; N, 19·0; OMe, 8·8; NMe, 7·9%). It is sparingly soluble in cold water, methyl or ethyl alcohol.

4(5)-*Carboxy*-1 : 3-*dimethylglyoxalinium picrate* crystallises from water in fine, yellow, anhydrous needles, m. p. 220—221° (corr.) (Found : C, 39·3; H, 3·2; N, 19·2; OMe, nil; NMe, 15·5. $C_{12}H_{11}O_9N_5$ requires C, 39·0; H, 3·0; N, 19·0; 2NMe, 15·5%). It is sparingly soluble in cold water or alcohol. This salt was also prepared by methylating pure methyl 1-methylglyoxaline-5-carb-

oxylate (1 g.) by heating with methyl sulphate (1 c.c.), hydrolysing the product with sodium hydroxide, and isolating the final product as picrate as previously described; yield, 54%.

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