

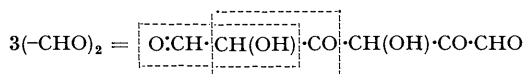
151. *Dibenzylidene- and Diisopropylidene-glyoxal.*

By HARRY RAUDNITZ.

Chemical evidence has been adduced in favour of structure (I; R = H, R' = Ph) and (I; R = R' = Me) for dibenzylidene- and diisopropylidene-glyoxal, respectively. This indicates that trimeric glyoxal, which is readily formed from monomeric glyoxal or from glyoxal sulphate, may have the structure (II).

SINCE Debus (*Annalen*, 1856, **100**, 5) discovered glyoxal our knowledge of this, the simplest of the dialdehydes, has been considerably increased, especially through the work of Harries and Temme (*Ber.*, 1907, **40**, 156). The monomer (CHO)₂ can be obtained but polymerizes instantaneously in presence of traces of moisture (even that normally present in the atmosphere) to a trimeric modification. This behaves similarly to the monomer, giving derivatives of the latter when treated with the appropriate reagents in aqueous or alcoholic solution. Derivatives of the trimeric form itself have not yet been recorded.

Since trimeric glyoxal reduces Fehling's solution, Harries concluded that it must contain a group to which the reducing power is directly attributable. In order to explain this behaviour he assumed the formation of an acyloin compound in which three molecules are joined as follows:

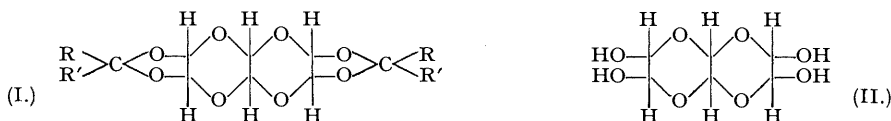


He further assumed that the groups enclosed by the broken lines are in fact the reducing groups, whilst the normal aldehyde groups of glyoxal itself have no reducing properties.

Because of these reducing properties Harries drew attention to the similarity between trimeric glyoxal and the sugars. The purpose of this investigation is to throw more light upon this relation. Just as sugars are able to form cyclic semiacetals, so glyoxal has a marked tendency to ring formation. In consequence, however, of the shortness of the carbon chain, condensed dioxan rings are obtained instead of the furanose or pyranose rings common in the sugars.

It is now shown that certain of the reactions which serve to characterise the sugars or sugar alcohols may be used with equal success for the preparation of derivatives of trimeric glyoxal, *e.g.*, the formation of *benzylidene* and *isopropylidene* derivatives by reaction respectively with benzaldehyde and acetone in presence of, *e.g.*, sulphuric acid.

Glyoxal sulphate reacts with benzaldehyde in presence of water to give a dibenzylidene compound of the empirical formula C₂₀H₁₈O₈, m. p. 268° (block), and similarly with acetone to give a diisopropylidene compound of the empirical formula C₁₂H₁₈O₈, m. p. 207° (block) (Raudnitz, *Chem. and Ind.*, 1944, 327,366; Dyson, *ibid.*, p. 342). Neither of these derivatives reacts with ketonic reagents, and with neither compound does the active-hydrogen determination disclose the presence of any hydroxyl groups. No coloration is given by these compounds with tetranitromethane or with ferric chloride and they must, therefore, be considered as saturated. On treatment with sulphuric acid each decomposes into its components. This behaviour seems



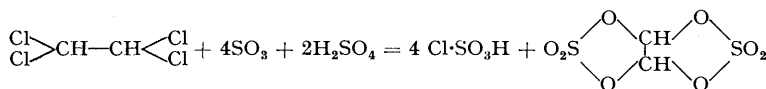
to be explained satisfactorily only by the structures (I; R = H, R' = Ph) and (I; R = R' = Me). On the basis of the results set out above, trimeric glyoxal itself must be considered as 2 : 3 : 6 : 7-tetrahydroxy-1 : 4 : 5 : 8-tetraoxadecahydronaphthalene

(2 : 3 : 6 : 7-tetrahydroxy-1 : 4 : 5 : 8-naphthadioxan) (II) with each pair of adjacent hydroxyl groups on the same side of the ring.

This structure accounts for the fact that trimeric glyoxal can react with ketonic reagents as though it were a true dialdehyde owing to the facility with which the oxygen ring is opened. On oxidation with hydrogen peroxide or potassium permanganate (Heimrod and Levene, *Biochem. Z.*, 1910, **29**, 33, 46) formic acid is produced, and not oxalic acid, as might have been expected had glyoxal reacted in the simple dialdehyde form. This also is explained by the proposed formula, since the oxidative attack may be assumed to be directed towards the glycol groupings with cleavage of the carbon-carbon bond. Finally, the structure also agrees with the optical properties of trimeric glyoxal which, in contrast to the monomer, has only a weak general absorption in the short ultraviolet.

Trimeric glyoxal can be considered as the simplest member of the osones. Like the osones it is amorphous and it may reasonably be assumed that the osones exist only in polymerized forms. It is intended to deal with this question at greater length in a further paper.

The glyoxal sulphate used in these experiments was prepared by a modification of the methods described in D.R.-P. 362,743 and B.P. 447,135, and the structure adopted here for glyoxal sulphate is that proposed by Baker and Field (*J.*, 1932, 86).



EXPERIMENTAL.

Glyoxal Sulphate.—To 60% oleum (400 g.; *i.e.*, 53% excess) and mercuric sulphate (2 g.) in a 1-l. conical flask was added tetrachloroethane (83 g.) in three equal portions with vigorous shaking at intervals of 5 mins., and the flask was loosely covered and set aside overnight. Next morning the contents were nearly solid through separation of a mass of needle-like crystals of glyoxal sulphate, but reaction was allowed to proceed for a further 8 days. The product was then filtered off, sucked as dry as possible, and added in small portions to ice-water with continuous stirring; the colourless needles were collected, washed thoroughly with water, and dried in a vacuum at room temperature; yield, 79 g. = 72% on the tetrachloroethane.

Dibenzylideneglyoxal.—Glyoxal sulphate (20 g.) was suspended in freshly distilled benzaldehyde (50 c.c.), and water (3 c.c.) added. The mixture was warmed gently on a steam-bath and then left at room temperature for 7 days, during which it set to a red solid. It was then diluted with alcohol, filtered off, and washed thoroughly with alcohol, the last traces of unreacted glyoxal sulphate being removed by short boiling with alcohol (50 c.c.), filtering, and washing with alcohol; yield, 9.5 g., 79.6%. *Dibenzylideneglyoxal* was recrystallised from glacial acetic acid, from which it separated in long, colourless needles, m. p. 268° (block) (Found: C, 62.0; H, 4.8. $\text{C}_{20}\text{H}_{18}\text{O}_8$ requires C, 62.1; H, 4.7%).

In order to determine the ratio of benzaldehyde to glyoxal, the compound was hydrolysed with dilute sulphuric acid by heating under reflux. After cooling the benzaldehyde was distilled off through a fractionating column, and determined as its *p*-nitrophenylhydrazone (Feinberg, *Amer. Chem. J.*, 1913, **49**, 105). In order to determine the glyoxal as formic acid (Friedemann, *J. Biol. Chem.*, 1927, **73**, 331), the residue in the flask was neutralised with barium carbonate, and the precipitate filtered off and washed thoroughly with water. The clear filtrates were combined and made up to a fixed volume. To an aliquot portion of this were added hydrogen peroxide and a measured excess of 0.1N-sodium hydroxide. After standing at room temperature for 10 mins., the excess of alkali was back-titrated with 0.1N-hydrochloric acid (Found: Ph·CHO, 55.4; $\text{C}_2\text{H}_2\text{O}_2$, 44.5. Calc.: Ph·CHO, 54.9; $\text{C}_2\text{H}_2\text{O}_2$, 45.1%).

Diisopropylideneglyoxal.—Glyoxal sulphate (20 g.) was dissolved in acetone (100 c.c.), water (3 c.c.) added, and the mixture left for 2 days. The crystals were filtered off, and washed successively with water, alcohol, and ether. Recrystallised from acetone, diisopropylideneglyoxal was obtained in large, colourless leaflets, m. p. 207° (block) (Found: C, 49.7; H, 6.3. Calc. for $\text{C}_{12}\text{H}_{18}\text{O}_8$: C, 49.7; H, 6.2%). Elsner's method (*Ber.*, 1928, **61**, 2364) for the determination of acetone in acetone sugars was used to determine the acetone, and glyoxal was determined as formic acid in the solution left from the distillation after removal of the sulphuric acid with barium carbonate (Found: COMe_2 , 39.6; $\text{C}_2\text{H}_2\text{O}_2$, 59.5. Calc.: COMe_2 , 40.0; $\text{C}_2\text{H}_2\text{O}_2$, 60.0%).

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