potassium iodide and a reflux condenser was attached by a ground joint. The mixture was boiled gently on a steam cone. At intervals 25 cc. of the reaction mixture was removed with a pipet, diluted with 250 cc. of water and titrated with 0.03620 *N* sodium thiosulfate, using starch solution as an indicator. At seventeen, twenty-three and twenty-nine hours, 41.7, 46.3 and 46.0% of bromine, respectively, were removed from the polymer.

A solution of 1.677 g. of the brominated polymer in acetone was made up to exactly 50 cc. The solution was placed in a glass-stoppered Erlenmeyer flask containing 1.0 g. of powdered potassium iodide. The flask, which was allowed to stand at room temperature, was shaken occasionally. At intervals 10-cc. samples were removed, diluted with 125 cc. of water and titrated with 0.03620 *N* sodium thiosulfate.

Under these conditions the percentages of bromine removed from the polymer were 25.9, 26.8, 32.2 and 32.1 after twenty-one, twenty-four, forty-five and seventy-nine hours, respectively.

Attempted Bromination of Polymethacrylyl Chloride.—A sample of polymethacrylyl chloride was obtained through the courtesy of Dr. B. C. Pratt of the du Pont Experimental Station. Four grams of this polymer was dissolved in 50 cc. of phosphorus oxychloride contained in a 100-cc. flask and 3.2 cc. of bromine was added. A reflux condenser protected by a calcium chloride tube was attached to the flask by a ground joint, and the mixture was irradiated for eight days with light from a 100-watt lamp. The product, isolated by the methods employed for the brominated polyacrylyl chloride, was 2.2 g. of brittle, brown solid.

Anal. Found: Br, 0.23.

Summary

Polyacrylyl chloride has been brominated and then esterified to give a polymeric bromoacrylic ester which liberated iodine from potassium iodide solution. This indicates that polyacrylyl chloride has some of its units arranged in a "head to head, tail to tail" fashion.

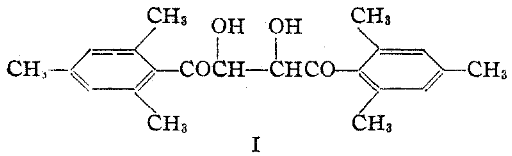
URBANA, ILLINOIS RECEIVED AUGUST 4, 1939

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

1,2-Diacylethylene Glycols

BY REYNOLD C. FUSON, C. H. MCBURNEY AND W. E. HOLLAND

Mesitylglyoxal reacts with the binary mixture, Mg + MgI_2,[1] in a very remarkable fashion; the reduction is entirely bimolecular, yielding 1,2-dimesitoylethylene glycol (I).[2] In the present work *t*-butylglyoxal, phenylglyoxal, 3,5-dibromomesitylglyoxal, 2,4,6-triethylphenylglyoxal and isodurylglyoxal have been found to behave in this same manner. In each case the product is the corresponding 1,2-diacylethylene glycol



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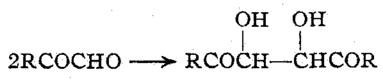
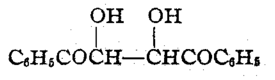


$$2\mathrm{RCOCHO} \longrightarrow \mathrm{RCO}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{H}-\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCOR}$$

The hindered glyoxals gave only one glycol while phenylglyoxal yielded two—presumably diastereoisomers



$$\mathrm{C_6H_5CO}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{H}-\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCOC_6H_5}$$

Thus it would seem that while steric hindrance is not responsible for the success of the reaction it may influence its course.

Two of the glyoxals, isodurylglyoxal and 3,5-dibromomesitylglyoxal, have not been reported before. They were made from acetoisodurene and 3,5-dibromoacetomesitylene, respectively, by treatment with selenium dioxide. The semicarbazones and the phenylhydrazones of the two glyoxals were prepared. The glyoxals were found to undergo rearrangement to the corresponding glycolic acids when treated with 10% potassium hydroxide solution.

The yield of glycol was found to depend on the time of reaction and on the ether–benzene ratio of the solvent. For example, in one experiment with phenylglyoxal, using an ether–benzene ratio of 1:2, the yield of glycol was only 2% of the theoretical; in another experiment in which an ether–benzene ratio of 2:3 was used the yield was 55%. If too long a reaction time is employed, side reactions occur. When mesitylglyoxal was treated with the binary mixture, Mg + MgI_2, for one hour the resulting glycol was contaminated with 1,2-dimesitoylformoin (II). In view of this fact a standard reaction time of fifteen minutes was used in all of the experiments.

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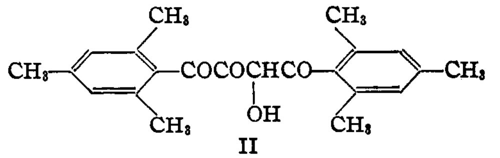
[1] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[2] Gray and Fuson, *ibid.*, **56**, 739 (1934).

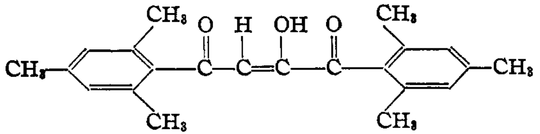


II

To see whether similar glycols might be produced from diketones, mesityl phenyl diketone was subjected to the reduction. The product was 2,4,6-trimethylbenzoin

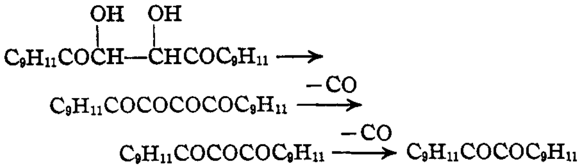
$C_9H_{11}COCH(OH)C_6H_5$

The bimolecular reduction product (I) of mesitylglyoxal underwent dehydration when treated with either oxalic acid or sulfuric acid, producing in both cases the same compound, 1,4-dimesityl-1,3,4-butanetrione enol (III). Likewise, the glycol gave an acetone compound when treated with acetone, magnesium sulfate and sulfuric acid.[3] Oxidation with lead tetraacetate gave mesitylglyoxal.



III

The glycol (I) also underwent oxidation with copper sulfate in pyridine, producing dimesityl diketone; oxidation with selenium dioxide gave dimesityl triketone. Dimesityl tetraketone was probably an intermediate in these reactions, carbon monoxide being lost to give first the triketone and then the diketone



$$C_9H_{11}CO\overset{OH}{C}H{-}\overset{OH}{C}HCOC_9H_{11} \longrightarrow C_9H_{11}COCOCOCOC_9H_{11} \xrightarrow{-CO} C_9H_{11}COCOCOC_9H_{11} \xrightarrow{-CO} C_9H_{11}COCOC_9H_{11}$$

An attempt was made to effect the transposition of a carbonyl group with an α-hydroxyl group by treatment with sodium ethoxide—a procedure which has been used with success by Henze[4] for similar compounds. Instead of the expected rearrangement product there was obtained 1,4-dimesityl-1,3,4-butanetrione enol (III).

The inability of the glycol to pass readily into the enol form was shown by the failure of attempts to prepare a tetraester. Treatment with four moles of ethylmagnesium bromide followed by four moles of acetyl chloride gave the formoin (II) instead of a tetraacetate; heating under reflux with benzoyl chloride according to the method of Lees[5] gave the benzoate of the enol (III) instead of a tetrabenzoate; treatment with sodium acetate and acetic anhydride gave an intractable oil.

Experimental

A. Glyoxals

3,5-Dibromomesitylglyoxal.—After 5.1 g. of selenium dioxide had been dissolved by warming in 100 cc. of wet dioxane, 14.5 g. of 3,5-dibromoacetomesitylene was added and the mixture refluxed for four hours. After most of the dioxane had been distilled, 250 cc. of toluene was added and the distillation continued until the distillate was no longer cloudy. The residual toluene was removed under reduced pressure. The glyoxal distilled at 157° (4 mm.); the yield was 41.5% of the theoretical. The **hydrate** melts at 100–102°.

Anal. Calcd. for $C_{11}H_{10}Br_2O_2$: Br, 47.90. Found: Br, 47.89.

The **semicarbazone** after several recrystallizations from alcohol and water melted at 238–241°.

Anal. Calcd. for $C_{12}H_{13}Br_2H_3O_2$: C, 36.83; H, 3.35. Found: C, 37.11; H, 3.71.

The **phenylhydrazone** crystallized from alcohol; m. p. 183–184.5°.

Anal. Calcd. for $C_{17}H_{16}Br_2N_2O$: C, 48.11; H, 3.77. Found: C, 48.44; H, 3.79.

3,5-Dibromomesitylglycolic acid was prepared by heating a suspension of the glyoxal hydrate with 10% sodium hydroxide solution. Acidification produced the white, crystalline acid which, after recrystallization from water, melted at 184–185°.

Anal. Calcd. for $C_{11}H_{12}Br_2O_3$: C, 37.53; H, 3.44. Found: C, 37.64; H, 3.39.

Isodurylglyoxal.—This glyoxal was prepared from acetoisodurene in 72% yield by the method just described; b. p. 123–127° (8 mm.). The hydrate melts at 86–87°.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.79; H, 7.36. Found: C, 75.90; H, 7.42.

The **semicarbazone** after recrystallization from alcohol melted at 207–208°.

Anal. Calcd. for $C_{13}H_{17}N_3O_2$: C, 63.16; H, 6.88. Found: C, 63.19; H, 7.19.

The **phenylhydrazone** crystallized from alcohol; m. p. 118–119°.

Anal. Calcd. for $C_{18}H_{20}N_2O$: C, 77.14; H, 7.14. Found: C, 76.92; H, 7.65.

Isodurylglycolic acid was prepared by heating the glyoxal hydrate with a solution of 10% potassium hydroxide. Acidification produced the white crystalline acid which, after recrystallization from water, melted at 171.5–172°.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.22; H, 7.69. Found: C, 69.48; H, 7.69.

The melting point of this acid is given by Claus and Foecking[6] as 156°. They obtained their product by the

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(3) Derx, *Rec. trav. chim.*, **41**, 316 (1922).

(4) Henze, *Z. physiol. Chem.*, **232**, 117 (1935).

(5) Lees, *J. Chem. Soc.*, **83**, 145 (1903).

(6) Claus and Foecking, *Ber.*, **20**, 3097 (1887).

reduction of isodurylglyoxylic acid. The acetoisodurene from which their glyoxylic acid was prepared may have been contaminated with acetoprehnitene and acetodurene, the isodurene used having been prepared by the action of methyl iodide and aluminum chloride on mesitylene. The isodurene used in the present experiments was made by the action of methyl sulfate upon mesitylmagnesium bromide.[7]

B. Glycols

1,2-Di-(2,4,6-triethylbenzoyl)-ethylene Glycol.—Seven grams of iodine was added in small portions to a warm mixture of 25 cc. of dry benzene, 17 cc. of dry ether and 2.5 g. of magnesium turnings; the additions were made through the condenser at such a rate as to keep the mixture just boiling. After the iodine had all been added and the initial vigorous reaction had subsided, the mixture was refluxed until the iodine color had disappeared. To this mixture, after cooling, was added 8.8 g. of 2,4,6-triethylphenylglyoxal. The flask was stoppered and shaken vigorously, with frequent cooling, for fifteen minutes, then the solution was decanted into 100 cc. of water, shaken and the magnesium hydroxide dissolved with dilute acetic acid. The organic layer was removed, washed with water and sodium thiosulfate solution, and the glycol was isolated by evaporation of the ether and benzene. After recrystallization from ethanol the glycol melted at 104–105° (corr.); yield, 3.7 g., which was 42% of the theoretical.

Anal. Calcd. for $C_{28}H_{38}O_4$: C, 76.66; H, 8.74. Found: C, 76.95; H, 8.81.

1,2-Di-3,5-dibromomesitoylethylene Glycol.—This glycol was obtained by the foregoing procedure in a 27% yield; m. p. 229–232°.

Anal. Calcd. for $C_{22}H_{22}O_4Br_4$: C, 39.42; H, 3.31. Found: C, 39.14; H, 3.64.

1,2-Di-(2,3,4,6-tetramethylbenzoyl)-ethylene Glycol.—Isodurylglyoxal gave a 37% yield of glycol; m. p. 160–161°.

Anal. Calcd. for $C_{24}H_{30}O_4$: C, 75.34; H, 7.92. Found: C, 75.65; H, 7.84.

1,2-Dipivalylethylene Glycol.[8]—*t*-Butylglyoxal was reduced in an atmosphere of nitrogen; otherwise the procedure was the same as that used for the three preceding glycols.

1,2-Dibenzoylethylene Glycol.—Reduction of phenylglyoxal gave two forms of 1,2-dibenzoylethylene glycol. These were separated by digesting the reduction mixture with small portions of ether until the residue had a constant melting point. In this way there was obtained from 19 g. of reaction mixture 3 g. of glycol melting at 125–127°. Although somewhat unstable this high-melting isomer could be recrystallized from ethanol by warming gently and stirring the mixture until solution was accomplished and then chilling the solution, m. p. 126–127.5° (corr.).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.09; H, 5.23. Found: C, 71.03; H, 5.46.

The **diacetate** of this glycol was prepared by refluxing with acetyl chloride for thirty minutes, pouring the reaction mixture into ice water and recrystallizing the solid from ethanol, m. p. 168–169° (corr.).

Anal. Calcd. for $C_{20}H_{18}O_6$: C, 67.75; H, 5.13. Found: C, 68.01; H, 5.21.

When the combined ether filtrates from the digestions were evaporated to one-half their volume and placed in the ice box, a mixture of crystals formed from which several crystals of the known isomer were separated by hand. The rest of the mixture was redissolved in ether and, after seeding with the hand-picked crystals, the solution allowed to evaporate to dryness. In this way 2 g. of the low-melting form of 1,2-dibenzoylethylene glycol was obtained which after recrystallization from ethanol melted at 118–119° (corr.).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.09; H, 5.23. Found: C, 71.28; H, 5.39.

This glycol was also prepared according to the general method of Milas and Sussman[9] using hydrogen peroxide and also by permanganate oxidation by a procedure based on that of Straus and Rohrbacher[10] for Δ'-dihydronaphthalene. Melting points of mixtures showed the products from the three sources to be identical.

2,4,6-Trimethylbenzoin.—The reduction of 5.04 g. of mesityl phenyl diketone with the binary mixture gave 1.5 g. of 2,4,6-trimethylbenzoin.[11]

C. Reactions of 1,2-Dimesitoylethylene Glycol (I)

Dehydration.—(a) Five-tenths gram of the glycol was dissolved in 5 cc. of concentrated sulfuric acid at 0° and allowed to stand at this temperature for thirty minutes. When the deep red solution was poured on ice, the solid enol separated and was isolated by filtration; it was purified by fractional crystallization from benzene, m. p. 112–113° (corr.). A mixture with an authentic sample of 1,4-dimesityl-1,3,4-butanetrione enol (III), prepared according to the method of Lutz,[12] showed no depression of the melting point.

(b) Four grams of the glycol was mixed thoroughly with 20 g. of hydrated oxalic acid and the mixture heated at 160° for four hours. At the end of this time the mixture was cooled and digested with hot water to remove the excess oxalic acid. The yellow enol (III), when recrystallized from ethanol, melted at 112–113° (corr.); yield, 3 g.

(c) A suspension of 3.5 g. of the glycol in 30 cc. of absolute ethanol was cooled to 0° and a solution of 0.23 g. of sodium in 10 cc. of absolute ethanol was added. The flask was closed with a cork and allowed to stand three hours at room temperature, with occasional shaking to prevent the suspension from settling out. The oil obtained by distilling the solvent at 30–40° *in vacuo* was dissolved in 50 cc. of ether and the solution washed with cold, dilute sulfuric acid and then with water. The residual oil obtained by driving off the ether was dissolved in the minimum amount of low-boiling petroleum ether and the solvent allowed to evaporate spontaneously. The residue consisted of yellow crystals covered with a yellow oil, which was removed by pressing the mass on a porous plate. The yellow enol after recrystallization from ethanol melted at 112.5–113° (corr.); yield, 1 g.

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(7) Smith, "Organic Syntheses," **11**, 66 (1931).

(8) This compound was made by Dr. H. W. Gray.

(9) Milas and Sussman, THIS JOURNAL, **58**, 1302 (1936).

(10) Straus and Rohrbacher, *Ber.*, **54**, 69 (1921).

(11) Fuson, Weinstock and Ullyot, THIS JOURNAL, **57**, 1803 (1935).

(12) Lutz, *ibid.*, **60**, 705 (1938).

The Acetone Compound.—The glycol when treated with acetone, concentrated sulfuric acid and anhydrous magnesium sulfate according to the method of Derx[8] gave the expected acetone compound, m. p. 117–118° (corr.).

Anal. Calcd. for $C_{25}H_{30}O_4$: C, 76.09; H, 7.67. Found: C, 76.03; H, 7.56.

Oxidation

(a) **Lead Tetraacetate.**—After 3.5 g. of the glycol had been dissolved in 100 cc. of dry chloroform 4.4 g. of lead tetraacetate was added in small portions to the well-stirred solution. At the end of two hours of stirring the insoluble lead acetate was removed by filtration, the solvent distilled and the residual mesitylglyoxal converted to the hydrate. The air-dried hydrate weighed 3.2 g.; yield, 91% of the theoretical. The glyoxal was identified as the phenylhydrazone, m. p. 136.5–137.5° (corr.).[13]

(b) Treatment of the glycol with copper sulfate and pyridine according to the method of Clark and Dreger[14] gave dimesityl diketone, m. p. 120–121°.

(c) After 10 g. of selenium dioxide had been dissolved by warming in 100 cc. of wet dioxane, 10 g. of the glycol was added and the mixture was refluxed for ten hours. One-half the dioxane was removed by distillation and the residue poured into 200 cc. of water. The solid product was dissolved in the minimum amount of low-boiling petroleum ether and the solution allowed to evaporate to dryness. After being freed from unchanged glycol by hand separation, the red dimesityl triketone melted at 110.5–111°; yield, 4.5 g. It was identified by a mixed melting point with an authentic sample.

Reaction with Phenylhydrazine.—After a solution of 2 g. of the glycol, 3 cc. of phenylhydrazine and 40 cc. of ethanol had been heated for forty-eight hours in a sealed tube on the steam cone, it was concentrated to one-half its volume and placed in the ice box overnight. The precipitate amounted to 1 g. of pale yellow crystals which, after three recrystallizations from ethanol, melted at 128–129° (corr.). The compound was not identified.

Anal. Calcd. for $C_{28}H_{28}O_2N_2$: N, 6.59. Found: N, 6.79.

Reaction with Benzoyl Chloride.—After refluxing 2 g. of the glycol with 10 cc. of benzoyl chloride for six hours the solution was cooled to 0° and poured into 10 cc. of cold methanol. The reaction mixture, after standing overnight in the ice box, was freed of the dibenzoate by filtration; the methanol and methyl benzoate were removed by distillation under reduced pressure. After the residue was dissolved in low-boiling petroleum ether and allowed to evaporate spontaneously, the yellow enol benzoate was separated by hand from the white dibenzoate of the glycol. The enol benzoate, after recrystallization from ethanol, melted at 141–142° (corr.) and was identified by a mixed melting point with an authentic sample of the benzoate of 1,4-dimesityl-1,3,4-butanetrione enol.

Anal. Calcd. for $C_{29}H_{28}O_4$: C, 79.05; H, 6.41. Found: C, 79.17; H, 6.73.

Treatment of the Glycol with Ethylmagnesium Bromide and Acetyl Chloride.—To a solution of 1.75 g. of the glycol in 40 cc. of benzene under nitrogen was added slowly with stirring an ether solution of ethylmagnesium bromide (4 moles). After refluxing the mixture for fifteen minutes, 5 cc. of acetyl chloride was added and the refluxing continued for thirty minutes. Removal of the solvents under reduced pressure left a few milligrams of the formoin (II) and an intractable oil. The formoin, after recrystallization from ethanol, melted at 187–188°; the melting point of a mixture with an authentic sample showed no depression.

Treatment of the Glycol with Sodium Acetate and Acetic Anhydride.—Two grams of the glycol was refluxed with 1 g. of anhydrous sodium acetate and 20 cc. of acetic anhydride for six hours. When the reaction mixture was decomposed with water an oil was obtained which could not be distilled or crystallized.

Summary

Five glyoxals have been reduced to the corresponding 1,2-diacylethylene glycols by the action of the binary mixture, $Mg + MgI_2$.

The properties of the glycol from mesitylglyoxal, 1,2-dimesitoylethylene glycol, have been described in detail.

URBANA, ILLINOIS RECEIVED SEPTEMBER 22, 1939

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[13] This melting point was erroneously reported as 145–146° by Fuson and Gray, *loc. cit.*

[14] Clark and Dreger, "Organic Syntheses," Coll. Vol. I, 1932, p. 80.