and β-L-allose,[6] as originally crystallized, were reported to melt, respectively, at 128–128.5° and 128–129°. Both of these sugars have now been found to exist in interconvertible dimorphous forms of m.p. 128° and m.p. 141°. The X-ray powder diffraction patterns of these crystalline phases are shown in Table I. DL-Allose was synthesized from its components and was found to crystallize as fine needles of m.p. 180°. The X-ray powder diffraction pattern exhibited by these crystals (Table I) was different from that of either of the dimorphs of β-D- (or β-L)-allose. Therefore the substance is a true racemic compound.

The crystalline D-,[7–10] L-[6,10] and DL-[10] forms of *ribo*-hexose phenylosazone[11] (*synonyms* allose, altrose, psicose, allulose phenylosazone) were freshly prepared and their X-ray powder diffraction patterns were ascertained (Table I). The racemic form again gives a pattern different from that of either component and is therefore a true compound. Good patterns are exhibited only by the freshly crystallized osazones and this fact may be used as further evidence that the phenylosazones can no longer be considered as derivatives of choice for the sugars. Clark and co-workers[12] report an X-ray powder diffraction pattern for a substance purported to be D-*ribo*-hexose phenylosazone.[11] Their data do not agree exactly with those which we record for either the DL or D form.

Experimental

Dimorphism of β-D-Allose and β-L-Allose.—A sample of β-D-allose, m.p. 128°, was found to have changed in melting point to 141° on storage. Its direction of mutarotation was unchanged. A sample of β-L-allose which had been stored for many years was found to still melt at 128° and its X-ray powder diffraction lines (Table I) were different from those of the higher melting form of β-D-allose. When the β-L-allose (m.p. 128°) was placed near a recently prepared sample of L-allose, it was converted to the higher melting (141°) form and the X-ray powder diffraction lines were then identical with those of β-D-allose (m.p. 141°). Recrystallization of the β-L-allose (m.p. 141°) from water–ethanol lowered the melting point to 130–131° and this preparation exhibited the X-ray powder diffraction lines characteristic of the lower melting form.

DL-Allose.—Accurately weighed equal amounts of the dimorphs (m.p. 141°) of β-D-allose and β-L-allose were recrystallized from water–ethanol; m.p. 180°, fine needles, X-ray powder diffraction lines recorded in Table I. The substance is a racemic compound.

(6) W. C. Austin and F. L. Humoller, *ibid.*, **55**, 2167 (1933); **56**, 1153 (1934).

(7) P. A. Levene and W. A. Jacobs, *Ber.*, **43**, 3141 (1910); P. A. Levene and F. B. LaForge, *J. Biol. Chem.*, **20**, 429 (1915).

(8) A. Kunz and C. S. Hudson, THIS JOURNAL, **48**, 2436 (1926).

(9) M. L. Wolfrom, A. Thompson and E. F. Evans, *ibid.*, **67**, 1796 (1945).

(10) Marguerite Steiger and T. Reichstein, *Helv. Chim. Acta*, **19**, 184 (1936).

(11) Nomenclature of J. C. Sowden, THIS JOURNAL, **69**, 1047 (1947).

(12) G. L. Clark, J. O. Gardner, L. Sattler and F. W. Zerban, *Sugar*, **47**, No. 5, 40 (1952).

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The Condensation of Chloropyruvic Acid with Chlorobenzene

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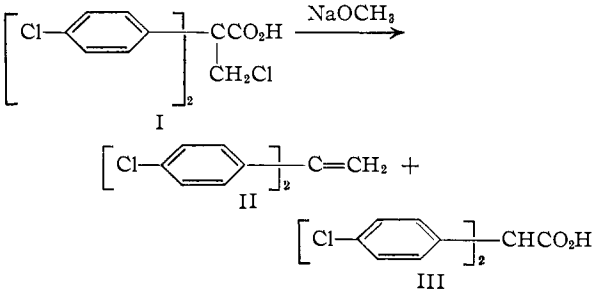
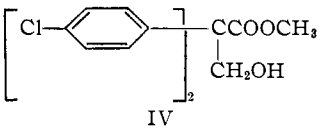
The sulfuric acid induced condensation of bromo- and chloropyruvic acids with benzene has been reported.[1,2] In this note the reaction of chloropyruvic acid with chlorobenzene to give a 33% yield of 2,2-di-(*p*-chlorophenyl)-3-chloropropanoic acid (I) is described. The *para* orientation of the halogen atoms was established by the fact that refluxing I with sodium methoxide in methanol followed by alkaline hydrolysis produced a mixture of the two known compounds, 1,1-di-(*p*-chlorophenyl)-ethylene (II) and di-(*p*-chlorophenyl)-acetic acid (III).



The formation of ethylenes of type II from anions of β-halocarboxylic acids is well known. The acid III, however, must be formed as a secondary degradation product of an intermediate β-lactone, which reacts under the experimental conditions to give the β-hydroxy ester IV. In the presence of



sodium methoxide this ester then suffers a reverse aldol cleavage to form the methyl ester of III.[3] Attempts to prepare the β-lactone by treatment of I with an equivalent amount of aqueous sodium hydroxide failed to produce an isolable product. In contrast, the unsubstituted 2,2-diphenyl-3-chloropropanoic acid gives almost a quantitative yield of the corresponding β-lactone under identical conditions.[4]

The acid I was only weakly insecticidal.

Acknowledgment.—The authors are indebted to Mr. E. F. Shelberg for the microanalyses.

Experimental

2,2-Di-(*p*-chlorophenyl)-3-chloropropanoic Acid (I).—To a suspension of 57 g. (0.46 mole) of chloropyruvic acid[5] in 450 cc. of concentrated sulfuric acid was added dropwise with stirring at room temperature 207 g. (1.84 moles) of chlorobenzene. After stirring at room temperature for 20 hours, the red solution was poured into ice, the precipitated oil was taken up in ether, washed well with water and dried over anhydrous magnesium sulfate. Filtration, removal of the ether by distillation, trituration of the residue with heptane and crystallation of the crude solid from an ether–pentane mixture gave 50 g. (33%) of condensation product I, m.p. 155–157°. Three more recrystallizations of a sample for analysis gave product of m.p. 157–158°.

Anal. Calcd. for $C_{15}H_{11}Cl_3O_2$: C, 54.65; H, 3.36. Found: C, 54.78; H, 3.28.

Treatment of 2,2-Di-(*p*-chlorophenyl)-3-chloropropanoic Acid (I) with Sodium Methoxide in Methanol.—To a solution of sodium methoxide prepared from 0.46 g. (0.02 gram-atom) of sodium in 60 cc. of dry methanol was added 3.3 g.

(1) J. Wegmann and H. Dahn, *Helv. Chim. Acta*, **29**, 415 (1946).

(2) H. E. Zaugg and B. W. Horrom, THIS JOURNAL, **72**, 3004 (1950).

(3) Compare H. E. Zaugg, *ibid.*, **72**, 3001 (1950).

(4) H. E. Zaugg, *ibid.*, **72**, 2998 (1950).

(5) M. Garino and I. Muzio, *Gazz. chim. ital.*, **52**, II, 226 (1922).

(0.01 mole) of the acid I and the mixture was heated at reflux for 24 hours. After removal of the methanol by distillation, the residue was heated under reflux for 1.5 hours with 70 cc. of a 10% aqueous solution of potassium hydroxide. On cooling, the insoluble oil solidified, was removed by filtration, washed and dried. There was obtained 1.5 g. of crude **1,1-di-(*p*-chlorophenyl)-ethylene (II)**, m.p. 80–85°, which on recrystallization from pentane gave colorless prisms, m.p. 84–86°.[6] A mixture of it with an authentic specimen of 1,1-di-(*p*-chlorophenyl)-ethylene[7] melted at 84–86°.

Anal. Calcd. for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05. Found: C, 67.75; H, 4.27.

The alkaline filtrate was acidified with hydrochloric acid, cooled and the precipitated **di-(*p*-chlorophenyl)-acetic acid** (III) (1.0 g., m.p. 163–167°) was removed by filtration, washed and dried. Recrystallization from 95% ethanol gave the pure acid, m.p. 165–166°.

Anal. Calcd. for $C_{14}H_{10}Cl_2O_2$: C, 59.81; H, 3.59. Found: C, 59.74; H, 3.45.

When mixed with an authentic specimen of III[8] it produced no depression of melting point.

(6) O. Grummitt, A. C. Buck and E. I. Becker, THIS JOURNAL, **67**, 2265 (1945), report m.p. 84–86°.

(7) Kindly supplied by Prof. Grummitt.

(8) O. Grummitt, A. C. Buck and R. Egan, *Org. Syntheses*, **26**, 21 (1946).

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The Preparation of 2-(α,β-Dihydroxyethyl)-benzofuran and 2-(α,β-Dihydroxyethyl)-coumaran

BY HAROLD E. ZAUGG

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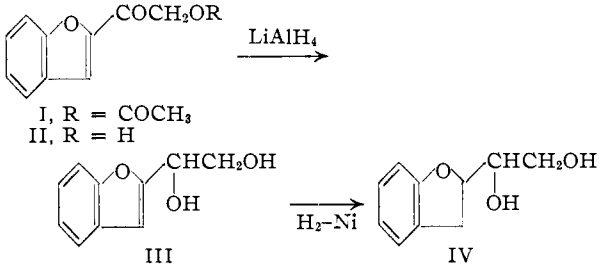
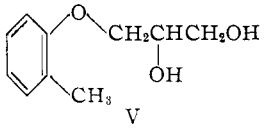
Shriner and Anderson[1] prepared ω-acetoxy-2-acetobenzofuran (I), but found that reduction of it either with sodium amalgam or with hydrogen in the presence of Adams catalyst resulted in cleavage to acetic acid and 2-acetobenzofuran. The present note reports the successful reduction of I with lithium aluminum hydride to 2-(α,β-dihydroxyethyl)-benzofuran (III), and further saturation of it by catalytic hydrogenation to 2-(α,β-dihydroxyethyl)-coumaran (IV), isolated as a mixture of diastereoisomers.



Compounds III and IV can be viewed as cyclized forms of the skeletal muscle relaxant, Mephenesin (V), formed by abstraction of hydrogen atoms from the *o*-methyl and α-methylene groups.



V

Both III and IV possess paralytic properties in mice; the activity of IV is comparable to that of V. In rabbits, however, IV is considerably less effective than Mephenesin.

As an incidental outcome of this work a by-product formed during the preparation of I was shown to be ω-hydroxy-2-acetobenzofuran (II) by its identity with an authentic sample prepared by treatment of ω-bromo-2-benzofuran with potassium formate.

Acknowledgment.—The author is indebted to Mr. Morris Freifelder for carrying out the catalytic hydrogenation, to Mr. E. F. Shelberg for the microanalyses, and to Dr. G. M. Everett for the pharmacological tests.

(1) R. L. Shriner and J. Anderson, THIS JOURNAL, **61**, 2705 (1939).

Experimental

2-(α,β-Dihydroxyethyl)-benzofuran (III).—To 2.7 g. (0.071 mole) of lithium aluminum hydride in 100 cc. of dry ether was added dropwise with stirring, a solution of 15.5 g. (0.071 mole) of ω-acetoxy-2-acetobenzofuran (I)[1] in 50 cc. of dry ether. The temperature was maintained below 10° until addition was complete, but the suspension was then stirred at room temperature for four hours. The mixture was decomposed by pouring carefully into ice containing an excess of hydrochloric acid. The ether was separated, washed with dilute sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation gave 10.2 g. (82.5%) of product, m.p. 80–85°. Two recrystallizations from benzene gave 9.4 g. of III in the form of colorless leaflets, m.p. 87–88°.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.48; H, 5.63.

2-(α,β-Dihydroxyethyl)-coumaran (IV).—A solution of 7 g. of III in 50 cc. of absolute ethanol was hydrogenated at 20 pounds initial pressure in the presence of 2.5 g. of Raney nickel. After filtration, and removal of the solvent by distillation, the residual oil was distilled *in vacuo* to give 4.6 g. (65%) of IV, b.p. 155–162° (1.5 mm.), $n^{25}D$ 1.5653. The product set to a semi-solid material which, after pressing between porous plates for several weeks, melted in the range 55–70°.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.72. Found: C, 66.65; H, 6.54.

The wide boiling and melting ranges of this material indicate that it is probably a mixture of diastereoisomers of IV.

ω-Hydroxy-2-acetobenzofuran (II).—A solution of 19.1 g. of ω-bromo-2-acetobenzofuran[1] in 400 cc. of 50% aqueous ethanol was refluxed for two hours with 26 g. of potassium formate and 2 cc. of concentrated hydrochloric acid. Pouring into ice, filtering and drying the resulting precipitate gave 12.6 g. of crude yellow product. A recrystallization from one liter of water followed by another from 50 cc. of 95% ethanol gave 5.9 g. of shiny colorless leaflets, m.p. 129–130°.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 68.08; H, 4.53.

This product proved, by mixed melting point determination, to be identical with the by-product obtained in only 2% yield during the preparation of I by the method of Shriner and Anderson.[1]

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The Bromination of Some N-Substituted Phthalimides with N-Bromosuccinimide

BY HAROLD E. ZAUGG

RECEIVED JULY 6, 1954

In 1898 Sachs[1] obtained N-bromomethylphthalimide in good yield by the high temperature (190°) bromination of N-methylphthalimide. However, N-ethylphthalimide, under the same conditions,

(1) F. Sachs, *Ber.*, **31**, 1225 (1898).