tion was refluxed gently and 35 g. of potassium permanganate, dissolved in 2 liters of water, added over a five-day period. The hot mixture was filtered and the residual manganese dioxide washed with hot water. The filtrate and washings were evaporated to a volume of 1 liter and acidified to congo red with hydrochloric acid. The small amount of precipitate which formed on standing consisted mainly of unoxidized nitrotoluenearsonic acid. It was removed by filtration and the filtrate evaporated to a volume of 100 ml. The desired arsonic acid crystallized from the solution and was purified by several recrystallizations from hot water.

3-Arsono-5-nitrobenzoic Acid, Acid Potassium Salt.—The procedure was similar to that described for the preceding compound. An aqueous solution of 8 g. of potassium permanganate was added to an aqueous solution of 5 g. of 5-nitro-*m*-toluenearsonic acid over an eight-hour period. The reaction mixture was warmed on the water-bath for eighteen hours, filtered, and the filtrate concentrated to 25 ml. The acid salt precipitated when this solution was acidified to congo red with hydrochloric acid. It was recrystallized from hot water.

2-Arsono-4-nitrobenzoic Acid.—The following procedure illustrates the general method that was employed for the preparation of the remaining six arsononitrobenzoic acids. 4-Nitroanthranilic acid (37 g.) was triturated with 200 ml. of concentrated hydrochloric acid, 100 ml. of water added, and the paste diazotized at 0–5°. A clear solution resulted.[12] A solution of 39.6 g. of arsenic trioxide in 80 ml. of 5 *N* sodium hydroxide was then added, dropwise, to the cold diazo solution, followed by the addition of 10 *N* sodium hydroxide until the mixture was faintly acid to congo red. The mixture was cooled overnight in the ice box and the precipitate which formed removed by filtration. This was dissolved in sodium bicarbonate solution, the solution filtered, and the filtrate acidified to congo red. The monosodium salt of the desired arsonic acid precipitated from solution. It was recrystallized twice from water. The free acid was obtained by recrystallizing this salt first from 2 *N* hydrochloric acid and finally from water.

4-Amino-2-dichloroarsinobenzoic Acid Hydrochloride.—4-Amino-2-arsonobenzoic acid (5 g.), prepared from the preceding compound by reduction with Raney nickel, was dissolved in 30 ml. of concentrated hydrochloric acid, 2 drops of 10% potassium iodide added, and reduced with sulfur dioxide. The crystalline precipitate which formed was washed with concentrated hydrochloric acid and recrystallized by dissolving in the minimum amount of water and adding concentrated hydrochloric acid. It was dried *in vacuo* over sodium hydroxide.

4-Amino-2-arsenosobenzoic Acid.—Ice-cold saturated sodium bicarbonate solution (15 ml.) was added dropwise to 3 g. of the above dichloroarsine. The resulting solid was washed with cold water until free from chlorides, and recrystallized from water. A similar procedure was employed for the preparation of the other seven arsenoso compounds.

The table lists the compounds prepared. We have included several compounds prepared by other workers or previously reported from this Laboratory in order to permit comparison of all the isomeric compounds in each class. Melting points were taken by the method described in paper VI of this series.[13] The method for taking melting points recently suggested by Morgan and Hamilton[14] was also used, and where the results by the two methods differed they are so indicated in the table. The arsononitrobenzoic acids were extremely stable substances, and vigorous and prolonged digestion was necessary in order to decompose these substances prior to analysis. With one compound, however, we were unable to obtain satisfactory analyses (ref. *b* to Table I).

Acknowledgment.—The authors wish to acknowledge the assistance given by Leon D. Freedman throughout the course of the work.

Summary

The preparation of isomeric arsononitro-, aminoarsono-, aminodichloroarsino- and aminoarsenosobenzoic acids is described. Evidence is presented which indicates that some of the previous descriptions of arsononitrobenzoic acids are incorrect. Analytical and descriptive data for nine arsononitro-, ten aminoarsono-, ten aminodichloroarsino- and eight aminoarsenosobenzoic acids are presented in tabular form.

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[12] In a few instances it was necessary to filter the solutions since several of the aminonitrobenzoic acids could not be diazotized completely even with an excess of sodium nitrite solution.

[13] Steinman, Doak and Eagle, THIS JOURNAL, **66**, 192 (1944).

[14] Morgan and Hamilton, *ibid.*, **66**, 874 (1944).

BALTIMORE 5, MD. RECEIVED JANUARY 8, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN AND THE ORGANIC CHEMISTRY DIVISION OF THE ORTHO RESEARCH FOUNDATION]

The Preparation of Ethyl α-Chloro- and α-Bromo-β,β-diethoxypropionates, and their Behavior in the Reformatsky and Darzens Reactions[1]

BY WILLIAM OROSHNIK[2] AND PAUL E. SPOERRI

In view of the fact that α-formylcarboxylic esters are hydrolyzed and decarboxylated on heating with water or dilute acids,[3–6] it might be expected that similar treatment of α-formylalkylideneacetic esters would yield α,β-unsaturated aldehydes. Since α-formylalkylideneacetic esters have never been reported in the literature, it was considered of interest to investigate their preparation.

Knoevenagel condensations were attempted with formylacetic ester and aldehydes and ketones, but in no instance could the desired reaction be effected. The self-condensation of formylacetic ester to formylglutaconic and trimesic esters and undistillable tars took place preferentially.[7] In order to prevent self-condensation,

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[1] This work is abstracted from the Dissertation of William Oroshnik presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn, June, 1944.

[2] Present address: Ortho Research Foundation, Linden, New Jersey.

[3] Tschitschibabin, *J. prakt. Chem.*, [2] **73**, 331 (1906).

[4] Wislicenus, *Ber.*, **20**, 2932 (1887).

[5] Wislicenus, Boklen and Reutke, *Ann.*, **363**, 347 (1908).

[6] Claisen, *ibid.*, **297**, 26 (1897).

[7] After this work had been completed, the report of Cogan (*Chem. Abs.*, **36**, 1301 (1942)) appeared describing unsuccessful attempts to effect aldol condensations between formylacetic ester and formaldehyde and acetaldehyde. He likewise found the products of self-condensation of formylacetic ester to preponderate.

similar experiments were carried out with the diethylacetal of formylacetic ester.[8] However, the methylene group in the acetal was found to be too inert to undergo condensation with carbonyl compounds.

Theoretically, a Reformatsky reaction of the acetal of a formylhaloacetic ester with an aldehyde or ketone should yield the desired α-formylalkylideneacetic ester; likewise, the epoxide resulting from a Darzens reaction of the same components should, on reduction and subsequent dehydration, yield the same product. In view of these considerations, the synthesis of the α-chloro, bromo, and iodo derivatives of ethyl β,β-diethoxypropionate was investigated. Wohl and Schweitzer[9] prepared the chloro compound by oxidizing the β-chlorohydrin of acrolein acetal and esterifying the resulting acid, but their method is long and tedious. In the present work, it was prepared in good yield by treating the potassium enolate of formylchloroacetic ester[10] with absolute ethanolic hydrogen chloride, and also by refluxing an absolute ethanolic solution of formylchloroacetic ester with ethyl orthoformate. Since formylbromoacetic ester cannot be obtained by the Claisen condensation of ethyl formate with ethyl bromoacetate,[10] it was prepared by the bromination of ethyl β,β-diethoxypropionate. It was also prepared by the addition of bromine to the sodium enolate of formylacetic ester in absolute ethanol, with subsequent addition of dry hydrogen chloride for acetal formation. Attempts to prepare the iodo derivative by refluxing its chloro or bromo analogs with alcoholic potassium iodide failed, and in each instance the acetal was recovered unchanged. The same treatment of the free chloroaldehyde resulted in the formation of the stoichiometric quantity of iodine. Further attempts to prepare the iodo derivative were abandoned.

Reactions which were carried out with ethyl α-bromo-β,β-diethoxypropionate, zinc dust, and various aldehydes and ketones proceeded smoothly, but in all cases, the only product isolated was ethyl β-ethoxyacrylate. This was identified by hydrolysis to the acid and a mixed melting point with an authentic sample of β-ethoxyacrylic acid. The relatively high yields of ethyl β-ethoxyacrylate indicate that the predominant reaction which took place was the removal of one ethoxy group and the halogen by zinc.[11] Since the undistillable residues contained no hydrolyzable material, it appeared unlikely that any of the desired reaction had occurred. The chloro compound did not react at all with zinc, but magnesium readily yielded β-ethoxyacrylic ester.

The Darzens reaction was tried with the chloro compound and acetophenone which is known to undergo such condensations readily. Instead of the expected epoxy compound a material was obtained which could not be purified but which responded readily to qualitative tests for enols. It is not unlikely that a Claisen condensation of the reactants occurred.

The behavior of ethyl α-chloro- and α-bromo-β,β-diethoxypropionate in the above reactions rather surprisingly indicates the lack of any of the halogen reactivity found in α-haloesters. The compounds appear to behave as α-haloacetals.

Experimental

Ethyl α-Chloro-β,β-diethoxypropionate. (a) Alcoholic Hydrogen Chloride Method.—To a well-stirred solution of 150 g. of dry hydrogen chloride in one liter of absolute ethanol on an ice-bath, 135 g. of the potassium enolate of ethyl formylchloroacetate ground to 80-mesh size was gradually added at a rate to maintain a temperature of 0–5°. The mixture was stirred for three hours at this temperature and for twenty-four hours at 25°. The inorganic salts were filtered off and washed thoroughly with absolute ethanol. The combined filtrate and washings were then concentrated through an efficient column at 35–40 mm., poured into 20% brine and finally extracted with ether. The ether solution, after drying over anhydrous potassium carbonate, yielded 100 g. of product boiling at 113–115° (15 mm.), (b. p. 102–104° (8 mm.), 107–109° (11 mm.)), $n^{19}\text{D}$ 1.4279.

Anal. Calcd. for $C_9H_{17}O_4Cl$: Cl, 15.78. Found: Cl, 15.91.

Wohl and Schweitzer[9] reported their product as boiling at 116–117° (11 mm.).

(b) **Ethyl Orthoformate Method.**—The oil precipitated by acidifying an aqueous solution of 135 g. of the potassium enolate of ethyl formylchloroacetate at 0° was taken up in ether. The ether solution, after thorough washing with 20% brine and drying over anhydrous magnesium sulfate, was concentrated under vacuum. To the concentrate were added 148 g. of ethyl orthoformate, 200 cc. of absolute ethanol and a few drops of concentrated hydrochloric acid and the mixture refluxed for two hours. Since the mixture was neutral at the end of this period, it was distilled directly; yield, 60 g. of the chloroacetal boiling at 113–115° (15 mm.), $n^{19}\text{D}$ 1.4275.

Ethyl α-Bromo-β,β-diethoxypropionate: (a) Direct Bromination of Ethyl β,β-Diethoxypropionate.—A few drops of bromine and a half cc. of pyridine were added to a well-stirred mixture of 150 g. of ethyl β,β-diethoxypropionate, 175 cc. of dry carbon tetrachloride and 120 g. of dry precipitated calcium carbonate. After stirring for fifteen minutes, the remainder of 135 g. of bromine was added dropwise during a period of two hours at 12–15°. Carbon dioxide evolved regularly and the mixture thickened considerably. (A very efficient stirrer was necessary to keep homogeneity in the porridge-like mass.) Stirring was continued for two hours at 12–15° after complete addition of the bromine. The mixture was then poured into ice-water and the excess calcium carbonate dissolved with hydrochloric acid. The carbon tetrachloride layer was removed, and after washing with water and dilute alkali and drying over anhydrous potassium carbonate, it yielded 118 g. of the bromoacetal boiling at 113–114° (9 mm.), $n^{20}\text{D}$ 1.4458.

Anal. Calcd. for $C_9H_{17}O_4Br$: Br, 29.69; C, 40.16; H, 6.37. Found: Br, 29.97; C, 39.94; H, 6.52.

(b) **Addition of Bromine to the Sodium Enolate of Ethyl Formylacetate.**—During a period of three hours,

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[8] Dyer and Johnson, THIS JOURNAL, **56**, 223 (1934).

[9] Wohl and Schweitzer, *Ber.*, **40**, 96 (1907).

[10] Wislicenus, *ibid.*, **43**, 3530 (1910).

[11] Although reports of similar reactions of bromoacetals have appeared in the literature, Krauze and Slobodin reported (*J. Gen. Chem.*, U. S. S. R., **10**, 907 (1940)) successful condensations of β-ionone with bromoacetal by means of magnesium to give 50–60% yields of β-ionylideneacetaldehyde. The authors have repeated this experiment several times and although no β-ionylideneacetaldehyde was ever obtained, there was no indication of vinyl ethyl ether formation; nor was any unreacted bromoacetal recovered.

222 g. of bromine was added at −10° to a well-stirred mixture of 200 g. of the sodium enolate of ethyl formylacetate in 1500 cc. of absolute ethanol. Anhydrous hydrogen chloride was then passed into the mixture at −10° until 170 g. was absorbed. Stirring was continued for three hours at −10° and for twenty-four hours at room temperature. The mixture was then worked up as described under ethyl α-chloro-β,β-diethoxypropionate, method "a"; yield, 76 g. of product boiling at 112–116° (9 mm.), n^{20}_{D} 1.4412.

On boiling with zinc dust in benzene, the compound readily yielded ethyl β-ethoxyacrylate.

Attempted Reformatsky Reaction between Ethyl α-Bromo-β,β-diethoxypropionate and Aldehydes and Ketones.—A few cc. of a mixture of 0.34 mole each of the bromoacetal and aldehyde or ketone (acetone, acetophenone, β-ionone, butyraldehyde, and benzaldehyde were tried) were added to 100 cc. of dry benzene containing some dissolved iodine and 26.4 g. of dry purified zinc dust. The mixture was partially immersed in an oil-bath at 70°, and stirred. Reaction soon commenced and the addition of reactants was then continued at a rate sufficient to maintain refluxing with the oil-bath at 70°. Refluxing was continued for three hours after complete addition of the reactants. The mixture was worked up in the usual manner and 39 g. of product boiling at 90–96° (16 mm.) was obtained.

The product was unsaturated as shown by a bromine test and, on hydrolysis with 10% caustic, it yielded an unsaturated acid melting at 109–110°. A mixed melting point with β-ethoxyacrylic acid prepared according to Tschitschibabin[3] showed no depression.

Attempted Darzens Reaction with Ethyl α-Chloro-β,β-diethoxypropionate and Acetophenone.—A suspension of dry sodium ethylate prepared from 5.7 g. of sodium wire in 250 cc. of anhydrous ether was added gradually at −10° to a mixture of 56 g. of chloroester and 29.7 g. of acetophenone. After stirring at 0° for eight hours, the dark brown solution was poured into ice-water, the ether layer separated, washed, and dried over anhydrous magnesium sulfate. It yielded a few grams of unreacted chloroacetal and acetophenone. The opaque aqueous layer, after clarification with Norite, gave a blue-red color with ferric chloride solution and deposited a heavy oil on acidification. The precipitated oil was soluble in alkali but insoluble in bicarbonate solution. On attempted distillation at 1 mm., it decomposed and resinified. A sodium fusion test indicated considerable chlorine.

Summary

1. New methods for the synthesis of ethyl α-chloro- and α-bromo-β,β-diethoxypropionates have been developed.
2. These compounds behave like α-haloacetals rather than α-haloesters in respect to their halogen activities.
3. Knoevenagel condensations could not be effected between formylacetic ester or its diethylacetal and aldehydes and ketones.

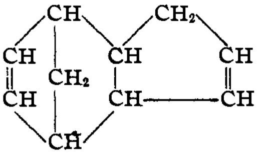
BROOKLYN, N. Y. RECEIVED SEPTEMBER 8, 1944

[CONTRIBUTION FROM RESINOUS PRODUCTS AND CHEMICAL COMPANY AND ROHM AND HAAS COMPANY]

The Chemistry of Dicyclopentadiene. I. Hydration and Rearrangement

BY HERMAN ALEXANDER BRUSON AND THOMAS W. RIENER

It has been shown by Alder and Stein[1] that dicyclopentadiene possesses an unsymmetrical structure (A)



(A)

which adds phenyl azide, nitrosyl chloride, or hydrogen to the double bond of the bridged cyclohexene ring. In each case the compounds obtained are normal addition products in which no rearrangement of the original ring system has occurred.[2]

We have found that various hydrogen donors notably water, HCl, HBr, HI, alcohols, phenols and carboxylic acids readily add to only one double bond of dicyclopentadiene. During these additions, which require the presence of hydrogen ions or acidic catalysts, for example H_2SO_4 or BF_3, a molecular rearrangement occurs to form an entirely different ring system.

When dicyclopentadiene is stirred rapidly with hot dilute sulfuric acid (20–40% H_2SO_4) it forms an unsaturated, secondary monohydric alcohol $C_{10}H_{13}OH$ in 80–84% yield. We have termed this alcohol hydroxy-dihydro-*nor*-dicyclopentadiene. It is a colorless liquid possessing a musty, somewhat camphoraceous odor, and does not solidify at 0°. With phenyl isocyanate it yields a crystalline phenylurethan melting at 164–165°.

The rest of the hydration product, in addition to resinous material, is the ether of hydroxy-dihydro-*nor*-dicyclopentadiene (II) having the formula $C_{10}H_{13}—O—C_{10}H_{13}$. This ether is a colorless liquid which is extremely autoxidizable. Thin films of it upon exposure to the air rapidly absorb oxygen to form a hard, brittle varnish. The pure di-(dihydro-*nor*-dicyclopentadienyl) ether can be obtained in quantity by treating hydroxy-dihydro-*nor*-dicyclopentadiene with one mole of dicyclopentadiene in the presence of sulfuric acid or boron trifluoride as a catalyst.[3] Upon catalytic hydrogenation this ether takes up four atoms of hydrogen to yield the saturated di-(tetrahydro-*nor*-dicyclopentadienyl) ether, a crystalline solid melting at 59–60°.

That the hydration of dicyclopentadiene by dilute sulfuric acid yields a rearranged alcohol instead of a normal hydration product such as (B) or (C) is borne out by the following discussion.

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(1) Alder and Stein, *Ann.*, **485**, 223 (1931).

(2) For a comprehensive survey of the present status of dicyclopentadiene chemistry see the review by P. J. Wilson and J. H. Wells, *Chem. Reviews*, **34**, 1–106 (1944).

(3) Bruson, U. S. Patent 2,358,314 (1944).