chloride, chloroform and carbon tetrachloride were photolyzed in monochromatic light of wave lengths 254 and 208 mμ. The molar percentage and the absorption of each component were always evaluated. All materials were highly purified, and air was rigorously excluded.

Hydrogen chloride was a product of every photolysis, and quantum yields based upon molecules of this substance formed per quantum absorbed by hydrogen sulfide were worked out for the various solutions and wave lengths. These were largest in carbon tetrachloride and smallest in methylene chloride. Quantum yields in pure methylene chloride, and chloroform, were determined similarly.

Enough of the reaction products in carbon tetrachloride were obtained for micro-fractionation and for identification of components by mixed melting point or by quantitative micro-analysis. These proved to be sulfur, hexachloroethane and trichloromethyl mercaptan. Qualitative evidence was available that analogous products were formed in the other two solvents.

Reaction mechanisms were worked out with due regard for thermodynamical considerations, by which the relative magnitudes, and in some cases the actual magnitudes, of quantum yields were accounted for. All reactions resulting from primary absorption of light by hydrogen sulfide can be interpreted in terms of the primary act $H_2S + h\nu \longrightarrow H + HS$ but not in terms of $H_2S + h\nu = H_2 + S$. Corresponding secondary reactions possibly initiated by the products of primary light absorption by carbon tetrachloride, also, were considered.

The temperature coefficients were normal, within experimental error.

CAMBRIDGE, MASS.

RECEIVED DECEMBER 31, 1937

[CONTRIBUTION FROM THE KENT AND GEORGE HERBERT JONES CHEMICAL LABORATORIES, THE UNIVERSITY OF CHICAGO]

The Preparation of *dl*-α,β-Diacetoxyisobutyric Aldehyde[1]

BY J. W. E. GLATTFELD AND WALTER E. MOCHEL

The preparation of the eleven theoretically possible C_4-saccharinic acids of molecular formula $C_4H_8O_4$ has now been accomplished.[2] This work was undertaken as a preliminary to the study of the saccharinic acid rearrangement of the tetroses. Work on the preparation of the tetroses by reduction of the corresponding tetronic acids is now being carried on as the next step in the rearrangement program.

The transformation of the C_4-saccharinic acids into the corresponding aldehydes would make available hydroxy aldehydes which might be of great usefulness in this study of saccharinic acid formation from sugars. Furthermore, these aldehydes would serve as sources for the preparation of some of the important C_5-saccharinic acids by means of the Kiliani reaction. It was for these reasons that the preparation of some of them was undertaken.

The work reported below was directed toward the preparation of the aldehyde corresponding to the acid first prepared by Glattfeld and Sherman and called by them *dl*-1,2-dihydroxyisobutyric acid.[3] A name for this substance more consistent with common usage is *dl*-α,β-dihydroxyisobutyric acid. This name henceforth will be used; in the present paper it will be shortened to α,β-iso acid.

Some success has been attained in the catalytic reduction of certain aldonic acid lactones in this Laboratory.[4] As acid lactones are internal esters, it was thought worth while to try the reduction of some of the esters of the α,β-iso acid. A series of the normal esters accordingly was prepared[5] and their reduction attempted. Catalytic reductions under widely varying conditions, with pressures from 30 to 2600 lb. (2 to 173 atm.) of hydrogen were tried. Sodium and sodium amalgams were also tried but neither the aldehyde nor the alcohol was obtained in any case. The apparatus used in these catalytic reduction attempts, and the general procedure, are described elsewhere.[6]

---

[1] This article is condensed from a dissertation presented by Walter E. Mochel in partial fulfilment of the requirements for the doctorate degree in The University of Chicago.

[2] Glattfeld and co-workers, THIS JOURNAL, **42**, 2314 (1920); **43**, 2675 (1921); **47**, 1742 (1925); **49**, 2309 (1927); **53**, 3164 (1931); **55**, 1114 (1933); **55**, 3663 (1933); **60**, 415 (1938).

[3] Glattfeld and Sherman, *ibid.*, **47**, 1742 (1925).

[4] Glattfeld and Shaver, *ibid.*, **49**, 2305 (1927); Glattfeld and Schimpff, *ibid.*, **57**, 2204 (1935).

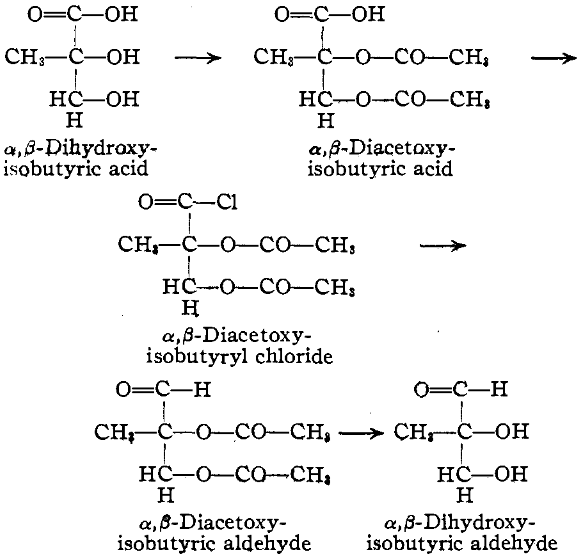
[5] Mochel, Masters Thesis, The University of Chicago, 1935.

[6] Glattfeld and Stack, THIS JOURNAL, **59**, 753 (1937).

While this work was going on, it was found that the reduction of the acid chlorides of aldonic and saccharinic acids to aldehydes held much more promise than the reduction of esters. The procedures of Rosenmund and others[7] were adapted to the work in hand and some success attained.

The present paper reports the preparation in pure condition of *dl*-α,β-diacetoxyisobutyric aldehyde. Forthcoming publications will report the preparation of the aldehydes corresponding to some of the other C_4-saccharinic acids. The authors feel sure that they also had in hand the unacetylated aldehyde, at least in solution. They were not able, however, to obtain this substance in the pure state.

The steps taken in the synthesis are outlined below. The α,β-iso acid was acetylated; the diacetyl acid was converted into the diacetyl acid chloride; this acid chloride was reduced catalytically; finally the acetyl groups were removed by hydrolysis. These steps are again indicated by the formulas below.


α,β-Dihydroxy-isobutyric acid

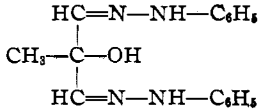
α,β-Diacetoxy-isobutyric acid

α,β-Diacetoxy-isobutyryl chloride

α,β-Diacetoxy-isobutyric aldehyde

α,β-Dihydroxy-isobutyric aldehyde

A simple phenylhydrazone of the free aldehyde could not be obtained, but a phenylhydrazine compound and a *p*-nitrophenylhydrazine compound were obtained which gave correct analyses for the dihydrazones. Normal osazone formation is obviously impossible because of the methyl group on the alpha carbon atom. Oxidation may have taken place on the primary alcohol group of the terminal carbon atom. If this assumption is correct, the structure of the resulting diphenylhydrazone would be



$$\begin{array}{l} \quad\;\; HC{=}N{-}NH{-}C_6H_5 \\ \qquad\; | \\ CH_3{-}C{-}OH \\ \qquad\; | \\ \quad\;\; HC{=}N{-}NH{-}C_6H_5 \end{array}$$

Further study of these dihydrazones is under way.

Experimental Part

Preparation of the Esters.—The methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl esters of the *dl*-α,β-iso acid were prepared in about 60-g. quantities. The same general method of esterification was used in each case. One-half mole of the acid was dissolved in 3.5 moles of the appropriate alcohol, heating if necessary for solution. Dry hydrogen chloride was passed into the cold solution until the weight of the solution had increased by about 3% of the weight of the alcohol used. The mixture was then refluxed for two hours, after which the excess alcohol and the hydrogen chloride were removed by distillation at 20 mm. pressure with a water pump. The residue was then completely distilled from the same flask at the same pressure. Small amounts of silver oxide were added to the distillate until no more whitening of the silver oxide occurred. The resulting mixture was then refluxed for fifteen minutes. The residue, consisting of unchanged silver oxide, silver chloride and ester, was transferred to a Claisen flask and fractionated at 10 mm. pressure with an oil pump.

The pure esters were all clear, colorless, oily liquids having a slightly ethereal odor. The methyl, ethyl, and propyl esters were very soluble, the butyl ester a little less soluble, and the amyl ester only slightly soluble in water.

The boiling points at 10 mm. pressure, together with the densities, the refractive indices, and the yields obtained in the preparations, are recorded in the accompanying table.

THE ESTERS OF *dl*-α,β-DIHYDROXYISOBUTYRIC ACID

Alcohol	B. p., °C. 10 mm.	d^{25}_4[a]	n^{25}_D[b]	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found	
Methyl	89	1.185	1.4438	68	$C_6H_{10}O_4$	44.78	44.60	44.67	7.46	7.56	7.54
Ethyl	95	1.1140	1.4370	71	$C_6H_{12}O_4$	48.65	48.72	48.48	8.11	8.09	8.28
n-Propyl	103	1.0789	1.4379	74	$C_7H_{14}O_4$	51.85	51.90	52.04	8.64	8.76	8.47
n-Butyl	113	1.0539	1.4393	80	$C_8H_{16}O_4$	54.55	54.21	54.57	9.09	9.16	9.12
							54.37			9.07	
n-Amyl	119	1.0288	1.4404	82	$C_9H_{18}O_4$	56.84	56.63	56.80	9.47	9.48	9.22

[a] Densities were measured by the pycnometer method. [b] Refractive indices were measured with an Abbé refractometer.

Attempts to Reduce the Esters.—The first attempts at reduction of the esters of the *dl*-α,β-iso acid to the corresponding aldehyde were made in a low-pressure hydrogena-

---

(7) Rosenmund, *Ber.*, **51**, 585, 594 (1918); Fröschel and Danoff, *J. prakt. Chem.*, **144**, 217 (1936); Cook and Major, THIS JOURNAL, **58**, 2410 (1936).

tor manufactured by the Burgess–Parr Company. Many different experiments were carried out using platinum and palladium catalysts under a wide variety of conditions of temperature, solvent, speed of agitation, promoters such as ferric chloride or iron, and oxygen-reactivated catalysts, but no aldehyde was detected even after four hundred hours. Reduction was then attempted at pressures of 2000 to 2600 lb. (133–173 atm.) of hydrogen, using the "Bomb B" described by Glattfeld and Stack.[6] After several attempts using a platinum catalyst with water or ethyl alcohol as solvent at various temperatures, reduction by means of the copper–barium–chromium oxide catalyst of Connor, Folkers and Adkins[8] was tried at a temperature below that normally used with this catalyst in the production of alcohols. Some of these experiments indicated that the corresponding alcohol was formed in very low yield.

Preparation of the Diacetyl-iso Acid.—The *dl*-α,β-iso acid was first acetylated in this Laboratory by Clay[9] and his method was used with a few alterations. To 130 g. of redistilled acetyl chloride in a 500-cc. flask attached to a reflux condenser carrying a calcium chloride tube was added 50 g. of the recrystallized acid of melting point 104°. (If more than 50 g. of the acid is used in one operation the decomposition during the subsequent distillation markedly reduces the yield of diacetyl acid.) After the action had subsided, the mixture was refluxed gently for two hours and then fractionated at 2 mm. pressure. The fraction which boiled at 135–145° was collected. This material was a viscous colorless liquid which only rarely crystallized. Redistillation at 2 mm. pressure gave a product which always solidified into beautiful shiny crystals if kept in a vacuum desiccator for several days. After having been dried for a week in the desiccator, these crystals melted at 59°. Clay reported a melting point of 57°. The yield of the solid varied from 25 to 30%.

The acid is very soluble in all the common solvents. Several attempts to recrystallize it from ether, using dry ice and acetone, were made without success.

Anal. Calcd. for $C_8H_{12}O_6$: sap. equiv., 68.0. Found: sap. eq., 68.4, 68.1.

The chief difficulty in the preparation of this diacetylated acid seemed to be in the purification step. Much of the material decomposed during distillation, leaving a brown gummy residue in the flask.

Other methods of acetylation gave yields which were no higher. Acetylation with acetic anhydride and the usual catalysts, pyridine, anhydrous zinc chloride, anhydrous sodium acetate and sulfuric acid, gave lower yields than acetylation with acetic anhydride alone.[9] Acetylation with acetyl chloride and pyridine gave yields no higher than when acetyl chloride was used alone. The acetylation method of Upson[10] was tried but again the yields were no higher. It was discovered, however, that the amyl ester could be acetylated in 90% yield with acetyl chloride according to the method of Franklin and MacGregor.[11] No procedure was found for removing the amyl group without also removing the acetyl groups of this compound and it proved, therefore, to be of no service. As it is new to the literature, its preparation and constants are reported here.

Preparation of the *n*-Amyl Ester of α,β-Diacetoxyisobutyric Acid.—Into a 3-necked flask, fitted with a mercury-seal stirrer, a reflux condenser, and a dropping funnel, was put 30 cc. of redistilled acetyl chloride and the flask and contents heated to 50° in a water-bath. Then 10 g. of the *n*-amyl ester of the *dl*-α,β-iso acid was added drop by drop after which the mixture was kept at 50° for ten minutes before being allowed to cool to room temperature. Stirring was continued all the while. The mixture which resulted was distilled at reduced pressure, first with a water pump to remove the excess acetyl chloride and finally with an oil pump. The fraction which boiled at 124° at 3 mm. pressure was a clear, colorless liquid weighing 13 g.

Anal. Calcd. for $C_{13}H_{22}O_6$: sap. equiv., 91.3. Found: sap. eq., 92.8.

Preparation of the α,β-Diacetoxyisobutyryl Chloride.—After several unsuccessful attempts at the preparation of the acid chloride by the use of thionyl chloride, phosphorus pentachloride was found to be quite satisfactory. Thirty grams of the diacetyl acid was added to a suspension of 35 g. of phosphorus pentachloride in 250 cc. of dry ether in a flask carrying a reflux condenser closed with a calcium chloride tube. This mixture was allowed to stand for twelve hours after which the excess phosphorus pentachloride was removed by filtration. The filtrate was run directly into the distilling flask from which it was to be fractionated. The ether and phosphorus oxychloride were then removed by distillation with a water pump and a water-bath at 50°. Distillation of the residue at 4 mm. pressure with an oil pump gave 19 g. of the acid chloride which distilled at 92–97°. This is a 58% yield.

The acid chloride was a colorless, limpid liquid only very slightly soluble in water. It reacted with water, however, when the mixture was warmed slightly.

Anal. Calcd. for $C_8H_{11}O_5Cl$: sap. equiv., 55.6; Cl, 15.93. Found: sap. equiv., 55.2, 55.7; Cl, 16.05, 15.72.

Preparation of the α,β-Diacetoxyisobutyric Aldehyde.—Eight grams of the acid chloride was dissolved in 50 cc. of sodium-dried, thiophene-free benzene, 0.1 g. of palladium oxide catalyst[12,13] added, and the mixture put into a 200-cc. 2-necked flask. Through one neck of the flask was inserted the hydrogen delivery tube, which passed to the bottom of the flask. To the other neck was attached a reflux condenser. Commercial electrolytic hydrogen was passed through a calcium chloride tower and into the flask rapidly enough to keep the catalyst uniformly suspended in the liquid. The hydrogen was passed in for seven hours although the evolution of hydrogen chloride had practically ceased after five hours. The solution was then filtered to remove the palladium catalyst and fractionated at 25 mm. pressure. After the benzene had passed over at 30°, the temperature rose and the diacetyl aldehyde distilled at 95–99°. This fraction was then redistilled at 30 mm. pressure and 5 g. of material was obtained which boiled at 104° under this pressure. This represents a yield of 74% of the theoretical.

---

(8) Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1138 (1932).

(9) Clay, Master's Thesis, The University of Chicago, 1932.

(10) Upson, THIS JOURNAL, **58**, 2549 (1936).

(11) Franklin and MacGregor, *J. Chem. Soc.*, **63**, 1421 (1893).

(12) Adams and Shriner, THIS JOURNAL, **46**, 1683 (1924).

(13) During the course of the work on this reduction it was found that the platinic oxide monohydrate catalyst of Adams, Voorhees and Shriner is just as effective as the palladium oxide catalyst.

Anal. Calcd. for $C_8H_{12}O_5$: C, 51.06; H, 6.38; sap. equiv., 94.05. Found: C, 50.74; H, 6.60; sap. equiv., 94.2, 94.3.

The diacetyl aldehyde is a water-soluble, colorless liquid with a pleasant odor.

Hydrolysis of the Diacetoxy Aldehyde.—Four grams of the diacetoxy aldehyde was dissolved in 100 cc. of 0.1 *N* sodium hydroxide solution and the solution boiled under reflux for thirty minutes. It was necessary to add more alkali from time to time to keep the solution alkaline. This alkaline solution was subjected to distillation at atmospheric pressure. A solution of what was apparently the dihydroxy aldehyde in water distilled from 100–104° leaving a residue of sodium acetate and alkali in the distilling flask. The aldehyde could not be separated from the aqueous phase by fractionation or by extraction. This hydrolysis procedure was also carried out in acid solution but the results were the same.

The aqueous distillate gave a red precipitate when warmed slightly with Fehling's solution. It also gave a silver mirror when heated slightly with Tollens' reagent. Sodium hydroxide was added to a portion of this aqueous solution until it contained about 10% of the hydroxide. This solution was boiled vigorously for ten minutes under a reflux condenser but there was no coloration of the solution and apparently no diminution of the reducing power of the solution. The aldehyde seems to be stable under these conditions.

Formation of a Diphenylhydrazone.—When a sample of the aqueous distillate which presumably contained the aldehyde was treated with an excess of phenylhydrazine in about 20% acetic acid solution, a few oily drops were formed. However, when the solution was kept at 100° on a water-bath for thirty minutes, a small amount of a slightly yellow precipitate was formed. This precipitate was separated by filtration, washed with water, and dried. It had a melting point of 144°, corr. The nitrogen analysis gave a value which checked fairly well with the theoretical for a diphenylhydrazone.

Anal. Calcd. for $C_{10}H_{14}O_2N_2$: N, 14.43; for $C_{16}H_{18}ON_4$: N, 19.86. Found: N, 20.66

Formation of a Di-*p*-nitrophenylhydrazone.—A sample of the aqueous solution of the aldehyde was treated with a 20% acetic acid solution of *p*-nitrophenylhydrazine. Even in the cold a very fine red precipitate was formed slowly. This precipitate was dissolved in the minimum amount of hot 95% ethyl alcohol. As the solution cooled slowly, a small amount of a very *dark* red precipitate was formed. This was separated and water was added to the filtrate until it was slightly cloudy. More hydrazine compound separated in the form of a *light* red precipitate. The latter did not have a definite melting point and was not purified further. The *dark* red precipitate, after having been dried, melted at 264°, corr. Again the analysis indicated a *dl*-*p*-nitrophenylhydrazone.

Anal. Calcd. for $C_{16}H_{16}O_5N_6$: N, 22.58; C, 51.60; H, 4.33. Found: N, 22.40, 22.60; C, 51.43; H, 4.48.

The *p*-Nitrophenylhydrazide of Acetic Acid.—This compound was prepared for comparison purposes. It was a white crystalline material with a sharp melting point at 205°, corr.

Anal. Calcd. for $C_8H_9O_3N_3$: N, 21.52. Found: N, 21.23, 21.43.

Summary

The preparation and some of the constants of the methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl esters of *dl*-α,β-dihydroxyisobutyric acid are reported.

It was not found possible to reduce these esters either catalytically or by means of sodium.

The *dl*-α,β-dihydroxyisobutyric acid was acetylated according to Clay's procedure by means of acetyl chloride to give 25–30% yields of the *dl*-α,β-diacetoxyisobutyric acid.

The *dl*-diacetoxy acid was then converted into *dl*-α,β-diacetoxyisobutyryl chloride by means of phosphorus pentachloride. The yields in this preparation were 50–60%. This acid chloride has not been reported in the literature.

The acid chloride was then reduced to the *dl*-α,β-diacetoxyisobutyric aldehyde in over 70% yield by means of both palladium and platinum catalysts. This substance is also new to the literature.

The *dl*-α,β-dihydroxyisobutyric aldehyde was obtained only in aqueous solution. Although the aldehyde is stable in both acid and alkaline solutions, it could not be separated in the pure state. The water solution of the aldehyde, however, gave compounds with phenylhydrazine and with *p*-nitrophenylhydrazine which analyzed correctly for dihydrazones.

CHICAGO, ILLINOIS RECEIVED FEBRUARY 28, 1938