lowing procedure seems to arise in the cleavage of monoacetoneglucose to 5-aldo-monoacetonexylose and the reduction of the latter to monoacetonexylose.

To a suspension of 5 g. of powdered D-glucose in 100 ml. of acetone at 0° there was added, dropwise, 4 ml. of sulfuric acid. The mixture was stirred in a closed flask (magnetic stirrer) for four hours at room temperature and then filtered from 140 mg. of unreacted D-glucose. The filtrate was made just alkaline by the addition, with shaking, of a 50% sodium hydroxide solution at 15–20° and filtered from the resulting sodium sulfate. After thorough washing of the salt cake with acetone, the combined filtrates were concentrated at reduced pressure, water was added and the concentration repeated to a volume of 50–75 ml. The solution was adjusted to *p*H 2.0 with concentrated hydrochloric acid and maintained at 40° with stirring for four hours. Following adjustment of the *p*H to 8–8.5 with sodium hydroxide, the solution was extracted with an equal volume (100–125 ml.) of benzene to remove unchanged diacetoneglucose. After addition of methyl red indicator, the aqueous layer was stirred with portions of powdered sodium metaperiodate while the *p*H was kept near that of the methyl red end-point by the dropwise addition of aqueous sodium hydroxide. When 7.3 g. of sodium metaperiodate had been added, starch–iodide paper indicated the presence of excess oxidant and the latter was destroyed by the addition of a few drops of glycerol. The solution was concentrated at reduced pressure, absolute ethanol added and the concentration repeated, and the sirupy residue, after addition of anhydrous sodium sulfate, was extracted with five 40-ml. portions of chloroform. Concentration of the extract at reduced pressure produced 5 g. of the crude acetonated dialdehyde. This was shaken, in 65 ml. of 95% ethanol, with hydrogen in the presence of 5 g. of Raney nickel for 90 hours at room temperature and atmospheric pressure. Following filtration and concentration, the residual monoacetonexylose was hydrolyzed by heating for one hour at 100° with 100 ml. of 0.1 *N* sulfuric acid. Acid was removed from the solution by ion-exchange, and concentration then yielded a residue of crystalline D-xylose. After grinding with cold 95% ethanol and filtration, there was obtained 2.35 g. (58%) of D-xylose, m.p. 144–147° and $[\alpha]^{25}\text{D}$ 19.1° equil. in water (*c* 9). These values agree well with the reported constants of pure D-xylose.

The rate of reduction of 5-aldo-monoacetonexylose with hydrogen and Raney nickel at room temperature and atmospheric pressure varies considerably with successive preparations of catalyst and acetonated dialdehyde. Absorption of hydrogen is complete in from 15 to 90 hours. In one experiment the reduction was carried out in a rocking autoclave at 75° and 1500 p.s.i. of hydrogen during four hours but no improvement in the yield (57%) of D-xylose was observed.

THE RADIOCHEMISTRY LABORATORY
DEPARTMENT OF CHEMISTRY
WASHINGTON UNIVERSITY
SAINT LOUIS, MISSOURI

RECEIVED MAY 25, 1951

α-Bromocitraconic Anhydride and α-Bromomesaconic Acid[1]

BY WYMAN R. VAUGHAN AND KIRBY M. MILTON[2]

Early attempts to prepare α-bromocitraconic anhydride and α-bromomesaconic acid were hampered by failure to appreciate fully the catalyzed *cis–trans* interconversion of ethylenic compounds, failure to understand the steric course of addition and elimination, and lack of suitable solvents for the purification of the products or intermediates. For example, Fittig found it necessary to crystallize DL-*threo*-α,β-dibromomethylsuccinic acid from water[3] in which it is 57% soluble at 13°, whereas nitromethane affords better than 81% recovery on recrystallization. Indeed this solvent appears to be an excellent crystallizing medium for many saturated as well as unsaturated α,β-dicarboxylic acids and anhydrides.

While the mechanism of the addition reaction is not a simple one,[4] in the present instance the picture of *trans*-halogen addition suggested by Roberts and Kimball[5] is satisfactory.

The elimination of halogen or hydrogen halide from a molecule may be pictured as essentially the reverse of addition,[6] the over-all result usually being *trans*-elimination. The present preparative procedures were designed in conformity with these generalizations.

The addition of bromine to the less stable *cis*-isomer is attended by danger of isomerization to the more stable *trans* form. Either acid (HBr) or radical (Br·) catalyzed isomerization may occur,[7] and therefore great care must be exercised to prevent formation of hydrogen bromide while appreciable citraconic acid is still present and to exclude light in order to minimize the dissociation of bromine into atoms.

Previous study[8] had shown that the addition of a few drops of bromine to a chloroform–ether solution of citraconic acid in sunlight afforded a 68% yield of mesaconic acid after only a few minutes; and while the desired addition could be accomplished in the dark, several weeks were required for its completion. In the present study, iodine, as predicted by other work,[9,10] proved to be an effective catalyst, the reaction reaching completion overnight in complete darkness. The yield of the desired dibromo acid could not be raised above 62%, since citraconic acid is not very soluble in chloroform at room temperature and the ether required to effect a homogeneous reaction mixture reacted with the bromine to produce some hydrogen bromide, which in turn effected some isomerization. Excess bromine did not affect the yield, but when the reaction was run in chloroform *alone*, heated to 50° to dissolve the citraconic acid, only insoluble mesaconic acid was obtained. The increase in temperature apparently was sufficient to provide energy for the formation of free halogen atoms which then catalyzed isomerization.

The preparation of α-bromomesaconic acid has been reported previously: once without procedural information[11] and once in considerable detail.[12] Significantly, the latter report includes a crude yield without melting point and a melting point of a pure sample without yield. It is stated simply that the compound was difficult to purify. Several attempts were made to repeat this work, and in no case was a yield of more than 13% of pure

---

[1] Abstracted from a portion of the Ph.D. dissertation of Kirby M. Milton, University of Michigan, 1951.

[2] Abbott Laboratories Fellow, 1949–1950.

[3] R. Fittig and P. Krusemark, *Ann.*, **206**, 2 (1881).

[4] P. W. Robertson, J. B. Butchers, R. A. Durham, W. B. Healy, J. K. Heyes, J. K. Johannesson and D. A. Tait, *J. Chem. Soc.*, 2191 (1950).

[5] I. Roberts and G. E. Kimball, THIS JOURNAL, **59**, 947 (1937).

[6] E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 118.

[7] For a comprehensive discussion of *cis–trans* interconversions with leading references, see G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 308.

[8] R. Fittig and C. F. Langworthy, *Ann.*, **304**, 145 (1899).

[9] W. Herz and B. Mylius, *Ber.*, **39**, 3816 (1906).

[10] L. Bruner and J. Fischler, *Z. Elektrochem.*, **20**, 84 (1914).

[11] A. Michael and G. Tissot, *Ber.*, **27**, 2130 (1894).

[12] W. Lossen and O. Gerlach, *ibid.*, **27**, 1851 (1894).

bromomesaconic acid obtained. The procedure involved treatment of DL-*threo*-α,β-dibromomethylsuccinic acid with concentrated alkali and, while this indubitably afforded the desired compound, several competing reactions (substitution of Br by OH, simultaneous loss of Br$^-$ and CO$_2$ etc.) interfered materially.

Consequently, dehydrobromination of the dimethyl ester of DL-*threo*-α,β-bromomethylsuccinic acid by pyridine was attempted. The results were most gratifying, yields as high as 93% being obtained. Saponification of the resulting ester readily afforded 86% of the desired acid.

Experimental[13]

DL-*erythro*-α,β-**Dibromomethylsuccinic Acid.**[14]—A mixture of 11.9 g. (0.86 mole) of mesaconic acid and 200 ml. of water was heated to boiling and 47.2 ml. (0.92 mole) of bromine was added over 45 minutes. The heating was continued for one-half hour, and the water was then removed by heating on a steam-bath under reduced pressure. The residue was slurried with water, filtered and washed with a little water; yield 83.3 g. (33.4%); m.p. 190–191° dec. On crystallization from chlorobenzene the product underwent some decomposition giving 55.1 g.; m.p. 187–188° dec. Nitromethane was later found to be an excellent solvent giving material which after a single crystallization melted at 196.5–197.5° dec. on slow heating (previously reported,[8] 193–194° on slow heating; 204° on rapid heating).

DL-*threo*-α,β-**Dibromomethylsuccinic Acid** (A).[8]—Two solutions, one of 57.00 g. (0.438 mole) of citraconic acid in 115 ml. of sodium-dried ether and 200 ml. of alcohol-free chloroform, and the other of 24.85 ml. (0.48 mole) of bromine and a few iodine crystals in 50 ml. of chloroform were mixed in a darkroom by the light of a small luminous flame. The reaction flask was stoppered and kept at room temperature in total darkness during the 17 hours required for complete disappearance of color. A considerable quantity of hydrogen bromide was observed when the flask was opened. The solution was evaporated in an air stream, and the residue was dried for 24 hours (*in vacuo*) over phosphorus pentoxide; yield 120.6 g. The oily residue was pressed on filter paper and washed with 150 ml. of benzene; 78.8 g. (62.0%); m.p. 148–149°. The product crystallized with 81% recovery from nitromethane in rectangular prisms; m.p. 153–153.5° (previously reported, 150–151°[8]).

(B).—A few iodine crystals were added to a solution of 6.72 ml. (0.131 mole) of bromine in 14.607 g. (0.1303 mole) of citraconic anhydride and the homogeneous solution was kept stoppered in total darkness for 7 days and then exposed to light for another 10 days. A precipitate began to accumulate gradually after 4 days. To the resulting dark mixture there was added 2.35 ml. (0.130 mole) of water. The crystalline mass, which formed rapidly with considerable evolution of heat, was not worked up for 2 months; but then the crude product (35.68 g.) was crystallized once from nitromethane; yield 26.82 g. (71.0%); m.p. 149–151°.

Methyl DL-*threo*-α,β-**Dibromomethylsuccinate.**—An ethereal diazomethane solution was added to 50.0 g. (0.172 mole) of DL-*threo*-α,β-dibromomethylsuccinic acid until the yellow diazomethane color persisted. The solution was then washed with a little 5% hydrochloric acid, water, 5% aqueous sodium bicarbonate, water, and then was dried over anhydrous calcium sulfate. After evaporation of the ether in a slow nitrogen stream the residue was vacuum distilled under nitrogen. A total of 53.114 g. (96.9%) boiling at 94–96° (1.8 mm.) was collected. Of this amount, 30.371 g. distilled at a constant temperature of 94.9° (1.8 mm.); $n^{25}{}_{\mathrm{D}}$ 1.4959.

Anal.[15] Calcd. for $C_7H_{10}Br_2O_4$: C, 26.44; H, 3.17; Br, 50.27. Found: C, 26.68; H, 3.26; Br, 50.05.

The product is a very pale yellow, fragrant, sweet-tasting liquid which is stable to hot aqueous alcoholic silver nitrate solution.

Bromocitraconic Anhydride.[16]—A mixture of 50 g. (0.172 mole) of DL-*erythro*-α,β-dibromomethylsuccinic acid and 25 g. of phosphorus pentoxide was heated slowly until the evolution of hydrogen bromide moderated. The semi-solid mass was then distilled to dryness at atmospheric pressure. The product distilled at 215–235° and rapidly solidified in the receiver; yield 30.8 g. (93%). The product was treated with Norit in carbon disulfide, and on concentration of the filtrate, 19.9 g. was obtained in five crops. A single recrystallization (from *ca.* 250 ml. of carbon disulfide) gave 15.2 g.; m.p. 100–101° (previously reported 100–101°[17]). The oily residues were not worked up even though a considerable amount of product remained in them.

Methyl Bromomesaconate.—A solution of 7.950 g. (0.0250 mole) of methyl DL-*threo*-α,β-dibromomethylsuccinate and 3.958 g. (0.050 mole) of pyridine was heated in an oil-bath at 120° for 10 minutes. The solution, which deposited crystals after 3 minutes and became very dark after 5 minutes, was cooled and extracted with water. The aqueous extract was acidified with 0.025 mole of nitric acid and titrated with silver nitrate and potassium thiocyanate showing that 51.2% of the bromine had been removed as bromide ion. The ester was dissolved in ether and the ethereal solution was dried over anhydrous sodium sulfate. Following the removal of the ether in a nitrogen stream, the ester was vacuum-distilled under nitrogen. Four clear, colorless fractions were collected over the range 85.9–89.0° (2 mm.); yield 4.604 g. (77.7%). The four fractions had refractive indices showing a spread of only 0.0006 unit, and no forerun and almost no residue were obtained. The second fraction was collected at 85.9–86.0° (2 mm.); b.p. 238° (734 mm.); $n^{25}{}_{\mathrm{D}}$ 1.4862.

Anal.[15] Calcd. for $C_7H_9BrO_4$: C, 35.46; H, 3.83; Br, 33.71. Found: C, 35.66; H, 3.94; Br, 33.49.

The reaction is exothermic, and when run on a 0.133 molar scale sufficient heat is developed, once the reaction starts, to afford an 81.2% yield without external heating. However, the yield was raised to 93.3% by increasing the heating period to 25 minutes, acidifying the cooled reaction mixture with sulfuric acid and extracting the ester with ether.

Bromomesaconic Acid.—A mixture of 0.790 g. (0.00333 mole) of methyl bromomesaconate and 0.40 g. (0.010 mole) of sodium hydroxide dissolved in 3 ml. of water was warmed on a steam-bath with stirring until the two layers became miscible (*ca.* 15 minutes). The solution was then cooled and extracted with ether. The dried ethereal extract on evaporation left no residue. The aqueous solution was acidified with 0.915 g. (0.010 mole) of concentrated nitric acid (sp. gr. 1.42), extracted with ether, and tested for bromide ion with silver nitrate with a negative result. The latter ethereal extract was dried over anhydrous calcium sulfate and evaporated leaving 0.597 g. (85.7%) of product; m.p. 197–216°. A single crystallization from nitromethane yielded 0.408 g.; m.p. 222.5–223° (previously reported[12] 220° after recrystallization of the zinc salt). A second crop of 0.040 g. was obtained on concentration of the filtrate after treatment with Norit.

---

[13] Melting points are corrected to ±0.5°.

[14] *Cf.* preparation of mesodibromosuccinic acid by H. S. Rhinesmith in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 177.

[15] Clark Microanalytical Laboratory, Urbana, Illinois.

[16] *Cf.* preparation of bromomaleic anhydride by P. Walden, *Ber.*, **30**, 2883 (1897).

[17] A. Angeli and G. Ciamician, *ibid.*, **24**, 74 (1891).

ANN ARBOR, MICHIGAN

RECEIVED MAY 3, 1951

A Method for Obtaining Approximate Pore Size Distribution Curves from Nitrogen Desorption Isotherms

BY LOWELL G. WAYNE

Barrett, Joyner and Halenda[1] have recently devised a numerical method for the approximate solution of Wheeler's integral equation[2] to give

---

[1] E. P. Barrett, L. G. Joyner and P. P. Halenda, THIS JOURNAL, **73**, 373 (1951).

[2] A. Wheeler, Presentations at Catalysis Symposia, Gibson Island A. A. A. S. Conferences, June 1945 and June 1946; reported in ref. (1).