washed well with U. S. P. chloroform. The filtrate was concentrated under reduced pressure and the white crystalline residue taken up in two liters of hot absolute ethanol. Upon cooling, the β-gentiobiose octaacetate separated as very pure white crystalline needles: m. p. 195–196° (corr.); yield 50.5 g., 74.1%.

α-*d*-Glucose-1,2,3,4-tetraacetate.—α-*d*-Glucose-1,2,3,4-tetraacetate was prepared in a manner similar to that of β-*d*-glucose-1,2,3,4-tetraacetate with the following exceptions. The chloroform extract of the tetraacetate was shaken with an ice-cold, saturated solution of sodium bicarbonate in order to remove all acetic acid. It was then washed with ice water, dried over anhydrous sodium sulfate, filtered and concentrated to a thick sirup. The concentrate was taken up in a small amount of methanol and the triphenylcarbinol allowed to separate out. After filtering, the methanol was removed under reduced pressure and the resulting sirup repeatedly taken up in chloroform, and reconcentrated. The sirup thus obtained was dissolved in dry ether and shaken with calcium chloride in order to remove any water or methanol still present. The sirup remaining after the removal of the ether under reduced pressure was used for the preparation of α-gentiobiose octaacetate.

α-Gentiobiose Octaacetate.—Thirty-eight grams of the α-*d*-glucose-1,2,3,4-tetraacetate sirup, silver oxide (15 g.), preheated "Drierite" (75 g.), iodine (5 g.), acetobromoglucose (20 g.) and dry, alcohol-free chloroform (300 cc.) were used in this preparation. The reaction was carried out according to the method described for β-gentiobiose octaacetate. The sirup obtained by concentrating the chloroform solution of the reaction products was taken up in absolute ethanol (250 cc.) and rubbed with a glass rod. Crystallization began after a few minutes. A yield of 50.9% (16.8 g.) of α-gentiobiose octaacetate was obtained. After two recrystallizations the product melted at 191–192° (corr.) and $[\alpha]^{29.5}\text{D}$ +51.6° (*c*, 4.29; *l*, 2; $CHCl_3$) C. S. Hudson and J. M. Johnson[12] reported a m. p. 188–189° (corr.) and $[\alpha]^{30}\text{D}$ +52.4° for the product obtained by the action of acetic anhydride and zinc chloride on β-gentiobiose octaacetate.

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Summary

1. An improved Königs–Knorr synthesis has increased the yield of β-gentiobiose octaacetate from 23.4 to 75–80% of the theoretical.
2. A 50% yield of α-gentiobiose octaacetate has been obtained by condensing acetobromoglucose with α-*d*-glucose-1,2,3,4-tetraacetate. So far as the authors are aware, this is the first time that a 6-linked α-octaacetate has been prepared by this method.
3. The complete synthesis of α- and β-gentiobiose octaacetates by this method may be completed in approximately one week.
4. Trityl bromide, a side product, has been introduced as a tritylating agent, thus decreasing both the time and cost of preparing the gentiobiose octaacetates.

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[12] C. S. Hudson and J. M. Johnson, THIS JOURNAL, 39, 1272 (1917).

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NOTES

The Activity Coefficient of Perchloric Acid, and a Correction to the Value of the Argentous-Argentic Oxidation Potential in Perchloric Acid

BY DON DEVAULT

The calculation of activity coefficients by Pearce and Nelson[1] from their measurements of the vapor pressure of perchloric acid solutions is apparently incorrect. Rosenfeld[2] has completely recalculated their data, obtaining results varying from 7.0% higher at 0.6 molal to 85.4% lower at 12 molal. Professor Redlich[3] has checked his values. Professor William C. Bray and I have also recalculated the data. The method which Pearce and Nelson report using gave us activity coefficients about 5% lower than those of Redlich and Rosenfeld. Although we examined a number of possibilities, we could not find the source of disagreement with Pearce and Nelson.

Our values of the activity coefficients agree with those of Redlich and Rosenfeld if we substitute, as did they, activity coefficients of hydrochloric acid for those of perchloric acid at 0.6 molal and lower concentration. This procedure receives justification from the electromotive force measurements of Popoff, Riddich, Wirth and Ough,[4]

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[1] Pearce and Nelson, THIS JOURNAL, 55, 3075 (1933).

[2] Landolt–Börnstein, "Physikalisch-chemische Tabellen," Erg. B. III, 2144 (1936).

[3] Private communication to Professor Bray. See also Redlich, Rosenfeld and Stricks, THIS JOURNAL, 58, 375 (1936).

[4] Popoff, Riddich, Wirth and Ough, *ibid.*, 53, 1195 (1931).

which show that $\gamma_{HClO_4} = \gamma_{HCl}$ up to 0.4 molal. The difference between the activity coefficients in dilute solution calculated from vapor pressure data directly and calculated from the more extensive hydrochloric acid data indirectly are probably due in the main to experimental error in the former measurements, for the assumption of errors of 0.001–0.006 mm. in the vapor pressure of water above the perchloric acid solutions in the points discarded would bring the calculations into agreement. We choose, therefore, the Landolt–Börnstein values as the most probable ones until more experimental work is done.

The Pearce and Nelson activity coefficient values were used to calculate the potentials of the hydrogen half-cells in perchloric acid and also of the perchloric–nitric acid liquid junctions in a series of researches by Professor A. A. Noyes and collaborators[5–9] on the oxidation potentials of strong oxidizing agents. The corrected activity coefficients lead to values of the argentous-argentic potential in 4 *m* perchloric acid[8] of **1.970** v. at 0.2° and **1.987** v. at 25.0°, changes of −12 and −13 mv., respectively. The corrections to the values in mixed nitric–perchloric acid solutions[8] have the small effect of changing the slope of the line in Fig. 2 (representing an average number of nitrates per silver atom in the argentic nitrate complex) from 1.6 to 1.5.

The hydrogen half-cell and the liquid junction potential corrections are of opposite sign and nearly cancel each other in the measurements of the argentous–argentic potential in nitric acid,[5,8] the cerous–ceric,[6] the thallous–thallic,[7] and the cobaltous–cobaltic[9] potentials in nitric acid. Dr. C. S. Garner[10] has corrected these potentials taking into account the newer Landolt–Börnstein values for the activity coefficient of nitric acid also. The over-all corrections range from −1.3 to +0.6 mv. and are probably negligible in view of the uncertainties in the liquid junction potentials. No other arguments or conclusions in these papers are affected by these changes.

I wish to acknowledge with gratitude the help and advice of Professor Bray, Dr. C. D. Coryell and Dr. C. S. Garner in preparing this note.

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(5) Noyes and Kossiakoff, THIS JOURNAL, **57**, 1238 (1935).

(6) Noyes and Garner, *ibid.*, **58**, 1265 (1936).

(7) Noyes and Garner, *ibid.*, **58**, 1268 (1936).

(8) Noyes, DeVault, Coryell and Deahl, *ibid.*, **59**, 1326 (1937).

(9) Noyes and Deahl, *ibid.*, **59**, 1337 (1937).

(10) Garner, Thesis, Calif. Inst. of Tech., 1938.

The Physical Constants of *cis*-Pentene-2

BY MARY L. SHERRILL AND ELIZABETH H. LAUNSPACH

In a recent article[1] the synthesis of *cis*-pentene-2 by the semi-reduction of pentyne-2 was reported. The designation of this pentene-2 as the *cis* form was based on the method of preparation and the assignment of structure was confirmed by its ultraviolet absorption in the Schumann region.[2] Because the quantity of the pentene-2 was insufficient for column fractionation, it was thought that there might be traces of pentyne present which would have the most marked effect on the boiling point and the density. The work has been repeated and the pentene-2 fractionated twice through a Fenske column (Column A). This column was 35 × 1.5 cm., with 1-turn 4-mm. glass helices. The reflux ratio for the two fractionations of the pentyne-2 was 1:20. The index of refraction was identical with that of the earlier preparation but the boiling point and the density were appreciably lower. The physical constants remained unchanged by the second fractionation and it is believed that the values so obtained constitute the most reliable data for the pure *cis*-pentene-2. Absorption spectrum measurements on this product gave no evidence of the presence of any of the *trans* isomer. These results therefore confirm the assignment of the *cis* structure to the higher boiling pentene-2, as is the case for the higher boiling isomer of butene-2.

The pentyne-2 was prepared in satisfactory yield from 2,3-dibromopentane by the action of alcoholic potassium hydroxide. This reaction takes place in two stages: the first being the formation of the pentyne-2 together with a mixture of 2-bromopentene-2 and 3-bromopentene-2. In the second stage of the reaction with more concentrated potassium hydroxide and prolonged heating at a higher temperature, these bromopentenes are converted into pentyne-2. In some cases appreciable amounts of pentyne-1 were also obtained; by further treatment with alcoholic potash this was transformed into pentyne-2. It is of interest to note that the 2,3-dibromopentane was prepared from pentene-2 which was a mixture of 25% of the *cis* and 75% of the *trans* isomer. In the course of fourteen different preparations of pentyne-2 there was always a 25% yield of pentyne-2 in the first stage of the reaction.

Half mole portions of a constant boiling frac-

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(1) Sherrill and Matlack, THIS JOURNAL, **59**, 2134 (1937).

(2) Carr and Stücklen, *ibid.*, **59**, 2138 (1937).