the structural formulas assigned above were correct. The physical constants are presented in Table I, and the infrared spectra[2] are shown in Figs. 1 and 2. The infrared spectra for perfluoropropyl disulfide and trisulfide are almost identical and indicate the similarities in structure. The main difference is the presence of a band at 12.59 microns for the trisulfide, absent for the disulfide, which may be accounted for by the presence of the additional sulfur atom in the former. In comparing these spectra with that for 1-iodoheptafluoropropane,[3] the striking similarity of all spectra from 2 to 9 microns is excellent evidence for the presence of the C_3F_3- group in all three cases.

The chemical reactions of these perfluoro sulfur compounds are being studied.

Experimental

In a sealed Pyrex glass bulb of 500-ml. capacity, a mixture of 22.0 g. (0.0743 mole) of 1-iodoheptafluoropropane prepared as previously described[3] and 50 g. of elemental sulfur was carefully heated at 250° for 14 hours. Reaction was evidenced by the liberation of large amounts of free iodine. Traces of a gaseous product were noted when the Dry Ice cooled flask was unsealed. There was finally collected 8.9 g. of iodine and 12.78 g. of a liquid product by transferring under a vacuum of 0.5 mm. at temperatures up to 180°. Fractional distillation at 760 mm. pressure yielded several cuts: 0.5 g., b.p. 41–45° (unreacted C_3F_7I); 0.5 g., b.p. approximately 90° (probably $C_3F_7SC_3F_7$); 7.0 g., b.p. 120–123°, mostly 122.2°, ($C_3F_7S_2C_3F_7$); and 3.0 g., b.p. 152.5–153° ($C_3F_7S_3C_3F_7$). *Anal.*[4] Calcd. for $C_6F_{14}S_2$: C, 17.92; F, 66.14; mol. wt., 402.2. Found: C, 17.89; F, 66.18; mol. wt., 400.0. Calcd. for $C_6F_{14}S_3$: C, 16.59; F, 61.25; S, 22.15; mol. wt., 434.3. Found: C, 16.30; F, 61.30; S, 22.35; mol. wt., 434.2.

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(2) Determined with a Baird Associates Infrared Recording Spectrophotometer of Samuel P. Sadtler and Sons, Inc., Philadelphia.

(3) M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951).

(4) Microanalysis by Clark Microanalytical Laboratory, Urbana, Illinois. Molecular weights determined by Victor Meyer method.

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PHILADELPHIA, PENNA. RECEIVED MAY 18, 1951

The Heat of Formation and Entropy of Aqueous Cuprous Ion

BY DONALD D. WAGMAN

The note by Hugus[1] has pointed out an error in the value of the entropy of aqueous cuprous ion in Table I–34 of the Selected Values of Chemical Thermodynamic Properties.[2] This value was calculated from the values for the heat and free energy of formation of the $Cu^+(aq)$ ion. In calculating the value of $\Delta H_f°$ we used the equilibrium data of Heinerth[3] on the reaction $^1/_2$ Cu (c) + $^1/_2Cu^{++}$ (aq) = Cu^+ (aq) measured as a function of temperature. However, the value ΔH = 9.4 kcal., calculated from the log K *vs.* $1/T$ plot, was erroneously assigned to the reaction Cu(c) + $Cu^{++}(aq)$ = $2Cu^+(aq)$. Utilizing the proper value of ΔH and the heat of formation of $Cu^{++}(aq)$ = 15.39 kcal./mole[2] (calculated from other data[4–7]) we obtain the following corrected values for the formation of $Cu^+(aq)$

$$Cu(c) + H^+(aq) = Cu^+(aq) + {}^1/_2H_2(g)$$
$$\Delta H_f°_{298.16} = 17.1 \text{ kcal./mole}$$
$$\Delta F_f°_{298.16} = 12.0 \text{ kcal./mole}^{8,9}$$
$$\Delta S°_{298.16} = 17.1 \text{ cal./deg. mole}$$

Taking the entropies of $H^+(aq)$, Cu(c), and $^1/_2H_2(g)$ as 0, 7.96, and 15.61 cal./deg. mole,[2] respectively, we obtain

$$S°(Cu^+(aq)) = 9.4 \text{ cal./deg. mole}$$

This value is in agreement with that of Hugus within the limits of uncertainty. The difference is due to the fact that we have assigned values to the heat and free energy of formation of the cupric ion $Cu^{++}(aq)$ slightly different from those used by Latimer, Pitzer and Smith in their calculation of the entropy of the ion.[10,11]

The values of $\Delta H_f°$ in Table I–34 for $Cu_2SO_4(aq)$ and $Cu(ClO_4)_2(aq)$ should also be changed to −181.4 and −47.4 kcal./mole, respectively.

We wish to thank Mr. Hugus for calling attention to this error.

(1) Z. Z. Hugus, THIS JOURNAL, **73**, 5459 (1951).

(2) Selected Values of Chemical Thermodynamic Properties, Series I, Table 34, National Bureau of Standards, Washington, D. C., (March 31, 1949).

(3) E. Heinerth, *Z. Elektrochem.*, **37**, 61 (1931).

(4) F. Muller and H. Reuther, *ibid.*, **47**, 640 (1941).

(5) F. E. Wetmore and A. R. Gordon, *J. Chem. Phys.*, **5**, 60 (1937).

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(7) A. Bouzat, *Ann. chim. phys.*, **29**, 305 (1903).

(8) F. Fenwick, THIS JOURNAL, **48**, 860 (1926).

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(10) W. M. Latimer, K. S. Pitzer and W. V. Smith, THIS JOURNAL, **60**, 1829 (1938).

(11) K. K. Kelley, Contributions to Theoretical Metallurgy. XI. Entropies of Inorganic Substances, U. S. Bureau of Mines Bull., No. 477 (1950).

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The Occurrence of Hydroxylysine in Proteins

BY LOIS WILEY INSKIP

Because of conflicting reports[1,2] in the literature on the occurrence of hydroxylysine in proteins, a search for hydroxylysine in the basic amino acid fractions of six protein hydrolysates was made by means of paper chromatography. Gelatin, known to contain about 1% hydroxylysine, was used as a control.

Two-dimensional chromatograms run in the phenol–collidine solvent system showed that hydroxylysine was present in gelatin, as was anticipated, but absent from casein, lactalbumin, glycinin and zein (gluten). Human hair contained a substance which moved on the chromatogram to a position very close to that occupied by hydroxylysine but which was probably cystine. Although cystine is usually decomposed during two-dimensional chromatography when phenol is used as the first solvent,[3] traces of it may be detected when it is

(1) D. D. Van Slyke, A. Hiller and D. A. MacFadyen, *J. Biol. Chem.*, **141**, 681 (1941).

(2) P. Desnuelle and S. Antonin, *Biochem. et Biophys. Acta*, **1**, 50 (1947).

(3) C. E. Dent, *Biochem. J.*, **43**, 169 (1948).

present in large amount, as it is in hair. When a chromatogram was run on a mixture of the hair basic amino acid fraction and known synthetic hydroxylysine, the hydroxylysine spot was observed to be in a position slightly different from that of any of the spots on the chromatogram of the hair basic amino acid alone, and to have a color distinct from the colors of the spots near it. Thus, it seems unlikely that hydroxylysine is present in human hair, at least in amount large enough to be readily detected by this method.

Chromatograms on the basic amino acid fraction of wool showed two spots close to the position occupied by hydroxylysine and having the same color as that exhibited by hydroxylysine. When a two-dimensional chromatogram was run on a mixture of the wool basic amino acids and known hydroxylysine, the hydroxylysine spot covered both of the spots observed on the chromatogram of the wool basic amino acids alone. In view of the report by Middlebrook[4] that hydroxylysine is present in wool, it seems quite possible that one of these spots might be hydroxylysine.

Experimental.—The proteins were hydrolyzed under nitrogen for 20 to 24 hours with 6 *N* hydrochloric acid. Excess hydrochloric acid was removed by treating the hydrolyzate with Amberlite IR-4B to *p*H 3.5. After removal of aromatic amino acids by the method of Partridge,[5] basic amino acids were adsorbed on a column of Amberlite IRC-50 buffered at *p*H 7.0. They were eluted from the column with 1 *N* hydrochloric acid, the eluate evaporated just to dryness, and taken up in water. The basic amino acids were separated from sodium chloride and other salts by precipitation with phosphotungstic acid, the phosphotungstates decomposed with 2 *N* hydrochloric acid, and phosphotungstic acid extracted with a mixture of amyl alcohol, ether and ethyl alcohol. The aqueous layer was then evaporated to dryness and taken up in a small amount of water for chromatography. The chromatographic solvents were an 80% solution of Merck and Co., Inc., reagent grade phenol in water, and Eastman Kodak Co. symmetrical collidine saturated with water. Ninhydrin, 0.25% in water-saturated *n*-butanol, was used as the color-developing agent.

(4) W. R. Middlebrook, *Nature*, **164**, 321 (1949).

(5) S. M. Partridge, *Biochem. J.*, **45**, 459 (1949).

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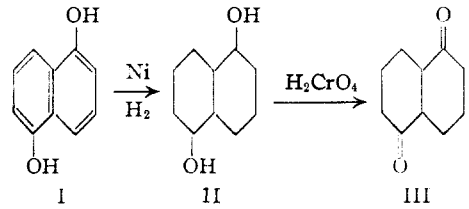
Decalin-1,5-dione

BY WILLIAM S. JOHNSON, C. DAVID GUTSCHE[1] AND D. K. BANERJEE[2]

Decalin-1,5-dione (III) is an intermediate in the total synthesis of estrone,[3] and has potential uses in other steroid syntheses.[4] It was prepared by Hudson and Robinson[5] by the hydrogenation of 1,5-dihydroxynaphthalene (I) over Raney nickel to decalin-1,5-diol (II), followed by chromic acid oxidation. Their procedure, however, was unsatisfactory because the diol could be obtained in only 5–8% yield, the chief product being α-decalols produced by hydrogenolysis.



I II III

In the present work the hydrogenation step was carried out over W-7 Raney nickel catalyst with added sodium hydroxide to avoid hydrogenolysis[6] and the mixture of stereoisomeric diols (II) was produced in over 70% yield. There are five diastereoisomeric forms of the diol II possible and two of these have been described previously: Campbell and Harris[7] synthesized an isomer, m.p. 178–178.5°, by catalytic reduction of an octalin-1,5-diol obtained by selenium dioxide oxidation of Δ^9-octalin. Hudson and Robinson[5] isolated what appeared to be a pure isomer, m.p. 159–161°, by repeated recrystallization of the mixture of diols II produced on catalytic hydrogenation. In our work a small amount of a new isomer melting at 210–211° was isolated from one of the hydrogenation runs.

Oxidation of the mixture of diols II with chromic anhydride in acetic acid gave a mixture of *cis*- and *trans*-decalin-1,5-dione in 60% yield.[5] In the present work a modified procedure was developed in which the oxidation was carried out with sodium dichromate and sulfuric acid in the presence of dilute acetic acid and benzene. Starting with the crude mixture of diols II, the mixture of diones III was obtained in over 70% yield. This mixture can be used directly for certain synthetic purposes,[3,4] or may be easily fractionated into fairly pure *cis* (m.p. 79–80° pure) and *trans* (m.p. 166–167° pure) isomers. The *cis* isomer has not been previously isolated. Since the *cis* is easily isomerized to the *trans* form,[5] the crude ketone mixture can be converted essentially entirely over to the latter by heating with acid.

Experimental[8]

Purification of 1,5-Dihydroxynaphthalene.—A solution of 600 g. of crude 1,5-dihydroxynaphthalene (Eastman Kodak Co., technical grade) in 3 l. of alcohol was boiled with 120 g. of Norit for 5 minutes, and filtered while hot. The insoluble tar and Norit remaining in the funnel were washed several times with boiling alcohol. The combined filtrates were again boiled with another 120 g. of Norit and 12 teaspoonfuls of Raney nickel, and filtered while hot. This filtrate was treated a third time with 60 g. of Norit and filtered yielding a straw-colored filtrate. Upon cooling to room temperature 234 g. of the diol crystallized. This material was separated by filtration. About 60 g. of Norit was added to the filtrate which was then concentrated by distilling off about 1 l. of the solvent (a rubber-sealed stirrer was employed to prevent bumping), filtered and chilled in the refrigerator. A second crop amounting to 108 g. was thus obtained. By repeating the concentration (Norit) and crystallization three times a total of 424 g. (71% recovery) of material suitable for hydrogenation was obtained.

(1) Wisconsin Alumni Research Foundation Postdoctoral Fellow, 1947. Washington University, St. Louis, Missouri.

(2) Watumull Foundation Fellow; W. A. R. F. Postdoctorate Fellow, 1948–1949. College of Engineering and Technology, Bengal, India.

(3) W. S. Johnson, D. K. Banerjee, W. P. Schneider and C. D. Gutsche, THIS JOURNAL, **72**, 1426 (1950).

(4) See for example, W. S. Johnson, J. Szmuszkovicz and M. Miller, *ibid.*, **72**, 3726 (1950).

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(7) W. P. Campbell and G. C. Harris, *ibid.*, **63**, 2721 (1941).

(8) Unless otherwise specified all melting points are corrected for stem exposure.