placed in 350 ml. of dry pyridine and heated to reflux temperature. The clear, hot solution was treated with 14 g. of I[6] and refluxed for 30 min. The clear, brown reaction solution was concentrated *in vacuo* and the residue treated with 2 l. of water, stirred, filtered, and the precipitate washed repeatedly with water. The precipitate was recrystallized from 10 l. of preheated (to boiling) 50% ethanol to yield fine, yellow needles (12.5 g.), m.p. 191–194° dec. One further recrystallization (almost quantitative) from 50% ethanol afforded pure material, m.p. 206–207° (to a brown liquid). Ultraviolet light absorption properties: in 50% ethanol, λ_{max} 225, 267, and 330 mμ, λ_{min} 255 and 289 mμ; $[\alpha]^{25}D$ −6° (*c* 0.30, in *N*,*N*-dimethylformamide).

Anal. Calcd. for $C_{17}H_{16}N_2O_7S_2$: C, 48.11; H, 3.80; N, 6.60; S, 15.11. Found: C, 48.04; H, 4.01; N, 6.94; S, 15.09.

1-(5′-O-Benzoyl-β-D-lyxofuranosyl)-4-thiouracil (III). The anhydro nucleoside II (5.0 g. in 400 ml. of 50% ethanol) was treated with 3.0 ml. of 1 *N* methanesulfonic acid and the mixture refluxed for 30 min. whereupon complete solution occurred. The yellow solution was refluxed for a total of 16 hr. Titration of an aliquot with alkali (Methyl Red indicator) indicated that the theoretical amount of methanesulfonic acid had been liberated. The solution was concentrated under vacuum to approximately 50 ml. whereupon yellow needle clusters separated (4.1 g.), m.p. 160° dec. Recrystallization from 25% ethanol gave analytical material, m.p. 169–171° dec. Light absorption properties in 50% ethanol: λ_{max} 230 and 331 mμ, shoulder at 265 mμ, λ_{min} 285 mμ. $[\alpha]^{25}D$ +127° (*c* 0.30, in *N*,*N*-dimethylformamide).

Anal. Calcd. for $C_{16}H_{16}N_2O_6S$: C, 52.74; H, 4.43; N, 7.69; S, 8.80. Found: C, 52.99; H, 4.88; N, 7.89; S, 9.13.

1-β-D-Lyxofuranosyl-4-thiouracil (V). The monobenzoate III (1.5 g.) was shaken in 75 ml. of 50% ethanol containing 5 ml. of *N* sodium hydroxide. After 1 hr., the clear solution was neutralized with acetic acid and concentrated to dryness *in vacuo*. The residue was taken up in water and treated batchwise with Dowex-50 (H^+) to remove sodium ion. The filtrate was then extracted three times with chloroform and the organic layer discarded. The aqueous layer was taken to dryness and the residue crystallized from hot ethanol. Recrystallization from 30 ml. of 90% ethanol gave analytical material, m.p. 198° dec., $[\alpha]^{22}D$ +71° (*c* 0.16, in *N*,*N*-dimethylformamide). Ultraviolet light absorption properties: in water, λ_{max} 250 and 331 mμ, λ_{min} 277 mμ.

Anal. Calcd. for $C_9H_{12}N_2O_5S$: N, 10.76; S, 12.32. Found: N, 10.81; S, 12.55.

1-β-D-Lyxofuranosylcytosine (IV). The monobenzoate III (1.4 g.) was placed in a tube containing *ca.* 50 ml. of ethanol previously saturated with ammonia at 0° and the tube sealed and heated at 100° for 12 hr. The tube was cooled, opened, and the contents concentrated to dryness. The residue was fractionated between water and chloroform and the aqueous layer taken to dryness. The red sirup was dissolved in ethanol with the aid of a few drops of water. Ethanol saturated with picric acid was added to the solution whereupon the *picrate of 1-β-D-lyxofuranosylcytosine* separated (1.34 g.), m.p. 207–208° dec. Recrystallization of 0.5 g. of the picrate from 100 ml. of 85% ethanol yielded a product of m.p. 208–209°.

Anal. Calcd. for $C_{15}H_{16}N_6O_{12}$: N, 17.79. Found: N, 17.20.

The *hydrochloride salt* of 1-β-D-lyxofuranosylcytosine was prepared from the picrate salt. Treatment of an aqueous solution of the picrate with Dowex-1 (Cl^-) batchwise afforded a colorless filtrate. The filtrate was concentrated *in vacuo* to dryness and crystallized from 90% ethanol, melting point begins to brown at 174° dec. and effervesces at 192°. $[\alpha]^{22}D$ +11° (*c* 2.0, in water). Ultraviolet light properties were akin to those reported for cytidine[15]; in *N* hydrochloric acid, λ_{max} 280 mμ, ϵ_{max} 13,110, λ_{min} 240 mμ, ϵ_{min}1080; at *p*H 7–12, λ_{max} 271 mμ, ϵ_{max} 9200, λ_{min} 249 mμ, ϵ_{min} 5600.

Anal. Calcd. for $C_9H_{14}N_3O_5 \cdot HCl$; C, 38.51; H, 5.38; N, 14.97; Cl, 12.63. Found: C, 39.08; H, 4.75; N, 14.82; Cl, 12.86, 12.90.

Conversion of IV *to 1-β-D-lyxofuranosyluracil* (VI). The hydrochloride salt IV (0.28 g.) was treated with an excess of dilute hydrochloric acid and of sodium nitrite and the solution allowed to remain at 40° overnight. Ionophoretic determination (0.1 *M* borate) showed that approximately 50% conversion to the uracil nucleoside had occurred. The aqueous solution was placed on a column (Dowex-50, H^+) and eluted with water until the eluate was free from ultraviolet absorbing material. The eluate was concentrated to a light sirup *in vacuo* (bath temp. ∽ 40°) and the sirup treated with ethanol. The ethanol was removed *in vacuo*. The ethanol addition and evaporation was repeated several times. The remaining light yellow sirup was dissolved in 10 ml. of 95% ethanol, cooled, and crystallized. The product, 1-β-D-lyxofuranosyluracil, (120 mg.) melted at 202.5–203.5° (reported,[5] m.p. 203–204°) and a mixed melting point with an authentic specimen[5] gave no depression.

1-(5′-O-Benzoyl-2′,3′-O-isopropylidene-β-D-lyxofuranosyl)-4-thiouracil. p-Toluenesulfonic acid (0.1 g.) was added to 0.1 g. of III dissolved in 10 ml. of acetone. The clear solution remained at room temperature for 30 min., after which it was concentrated *in vacuo* to *ca.* 5 ml. After addition of 5 ml. ethanol, the clear solution was cooled. Yellow rosettes crystallized (80 mg.), m.p. 195–200°. Recrystallization from 10 ml. of absolute ethanol afforded analytical material, m.p. 199–201.

Anal. Calcd. for $C_{19}H_{20}N_2O_6S$: C, 56.42; H, 4.98; N, 6.93; S, 7.93. Found: C, 56.53; H, 5.01; N, 6.86; S, 7.98.

Acknowledgment. The authors are indebted to Dr. George B. Brown for helpful discussions and continued interest.

DIVISION OF NUCLEOPROTEIN CHEMISTRY
SLOAN KETTERING INSTITUTE FOR CANCER RESEARCH
SLOAN-KETTERING DIVISION OF CORNELL UNIVERSITY MEDICAL COLLEGE
NEW YORK 21, N. Y.

(13) J. J. Fox, J. F. Codington, N. Yung, L. Kaplan, and J. O. Lampen, *ibid.*, **80**, 5155 (1958).

(14) E. R. Walwick, W. K. Roberts, and C. A. Dekker, *Proc. Chem. Soc.*, 84 (1959).

(15) J. J. Fox and D. Shugar, *Biochim. et Biophys. Acta*, 9, 369 (1952).

(16) All melting points are corrected unless stated otherwise. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Monosaccharide Sulfates. II. The Preparation of Methyl α-D-Glucopyranoside 2-Sulfate[1]

KENNETH B. GUISELEY AND PAUL M. RUOFF

Received October 26, 1961

It has been shown that the sulfation of glucose leads predominantly to the 6-sulfate.[2,3] Similarly, the sulfation of glucose derivatives having a free hydroxyl at the 6- position or at the 6- position and one or more others results in the formation of the

(1) Taken from a paper presented at the Chicago Meeting of the American Chemical Society, September 1961.

(2) Part I., *J. Org. Chem.*, 26, 1248 (1961).

(3) T. Soda and W. Nagai, *J. Chem. Soc. Japan*, **59**, 135 (1938).

6-sulfate.[2,4–8] In the course of our investigation it became of interest to sulfate a derivative of glucose which was readily available, had the 6- position blocked, and could be easily converted to glucose or a glucoside without cleaving the sulfate residue. Such a compound is methyl 4,6-*O*-benzylidene-α-D-glucopyranoside.

Jeanloz and Jeanloz[9] have investigated the problem from the standpoint of acetylation, benzoylation, and sulfonylation, finding that in certain cases, esterification occurred predominantly at the 2- position. Duff and Percival[10] sulfated methyl 4,6-*O*-benzylidene-α-D-glucopyranoside but did not isolate a pure product.

We have found that sulfation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside with pyridine-sulfur trioxide in *N*,*N*-dimethylformamide gave a 67% yield of barium methyl 4,6-*O*-benzylidene-α-D-glucopyranoside monosulfate. The latter was identified as the 2-sulfate by an unequivocal synthesis involving the intermediate methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 3-nitrate.[11,12] Following the sulfation of the methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 3-nitrate, the benzylidene group was removed by hydrolysis and the product converted to the brucinium salt. The resulting crystalline brucinium methyl α-D-glucopyranoside 3-nitrate 2-sulfate was dissolved in aqueous ethanol and the nitrate group removed by hydrogenolysis with palladium on charcoal.

The crystalline compound derived from the reduction step had a different x-ray pattern from that of brucinium methyl α-D-glucopyranoside monosulfate prepared by direct sulfation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside. However, when the latter was treated with hydrogen and palladium, one mole of hydrogen was consumed for each mole of the salt present. The compound isolated had the same x-ray pattern as that obtained by reduction of the glucoside nitrate sulfate. Similarly, when a solution of the compound prepared by the unambiguous method was passed over an Amberlite IR-120 column (hydrogen-ion form) and the effluent neutralized with alcoholic brucine, the compound formed had the same x-ray pattern as that prepared by direct sulfation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, thus establishing the latter's identity as the 2-sulfate. The first compound isolated after reduction was apparently one in which the double bond in the brucinium portion of the molecule had been hydrogenated.

Nitration of the amorphous material obtained by direct sulfation ultimately led to the isolation of two crystalline compounds. One of these proved to be brucinium sulfate; the other, not yet identified, is suspected of being brucinium methyl α-D-glucopyranoside 2,3-disulfate. No brucinium methyl α-D-glucopyranoside 3-nitrate 2-sulfate was isolated, nor was any product obtained which was suspected of being the 3-sulfate.

A study of the solvolytic reactions of methyl α-D-glucopyranoside 2-sulfate and the corresponding β-form will be reported in a forthcoming paper.

EXPERIMENTAL[13]

Methyl 4,6-O-benzylidene-α-D-glucopyranoside. Using the method of Freudenberg,[14] a mixture of 63.5 g. (0.33 mole) of methyl α-D-glucopyranoside, 50 g. of anhydrous zinc chloride, and 160 ml. of freshly distilled benzaldehyde was shaken for 5.5 hr. About 250 ml. of ice water was added and the mixture shaken vigorously. The precipitate was filtered off, triturated with 200 ml. of ice water, again filtered, and partially dried by aspiration under a rubber dam. It was then washed twice by trituration with 400-ml. portions of petroleum ether (b.p. 38–54°), followed by a further wash on the funnel. The crude product, after air drying, was dissolved in 650 ml. of nearly boiling water, filtered, and allowed to crystallize. The product was filtered off, washed with water, and dried in an oven at 110°; yield, 60 g. (65%). Its melting point was 166.5–167.5° (lit.,[14] 161–162°).

Sulfation of methyl 4,6-O-benzylidene-α-D-glucopyranoside. A solution of 28.3 g. (0.1 mole) of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside in 300 ml. of anhydrous *N*,*N*-dimethylformamide was placed in a 1-l. three-necked flask equipped with a ground-glass stirrer, drying tube, and dropping funnel. To the stirred solution was added a solution of 16 g. (0.1 mole) of pyridine–sulfur trioxide in 150 ml. of *N*,*N*-dimethylformamide over an 8-hr. period. Twenty-four hours from the start of the addition, the solution was warmed to 40°, then allowed to cool to room temperature. The solvent was removed *in vacuo* at less than 30°. The remaining sirup was taken up in 200 ml. of water and the solution quickly made basic to *p*H 11.0 with warm aqueous barium hydroxide. Carbon dioxide was then bubbled through the solution until the *p*H dropped to 7.1. Some antifoaming agent was added and the suspension concentrated to a paste *in vacuo*. After resuspension, the *p*H was still 7.1; the inorganic salts were centrifuged off and the solution filtered to remove the floating antifoam agent. The clear solution was concentrated to 40–50 ml. *in vacuo* and diluted with 450 ml. of absolute ethanol. Upon standing overnight in the refrigerator, the solution gelled. The gel was broken up and filtered, then washed with 98% ethanol by trituration, refiltered, and washed three times by trituration with anhydrous ether in an attempt to remove the

(4) H. Ohle, *Biochem. Z.*, **136**, 428 (1923).
(5) A. G. Lloyd, *Nature*, **183**, 109 (1959).
(6) B. Helferich, A. Löwa, W. Nippe, and H. Riedel, *Ber.*, **56B**, 1083 (1923).
(7) G. N. Bollenback, *Methyl Glucoside*, Academic Press, Inc., New York, 1958, p. 74 and references quoted there.
(8) S. Peat, J. R. Turvey, M. J. Clancy, and T. P. Williams, *J. Chem. Soc.*, 4761 (1960).
(9) R. W. Jeanloz and D. A. Jeanloz, *J. Am. Chem. Soc.* **79**, 2579 (1957).
(10) R. B. Duff and E. G. V. Percival, *J. Chem. Soc.*, 1675 (1947).
(11) (Mrs.) P. Szabo and L. Szabo, *J. Chem. Soc.*, 3762 (1960).
(12) J. Honeyman and J. W. W. Morgan, *J. Chem. Soc.*, 3660 (1955).

(13) (a) All melting points are uncorrected; (b) Microanalyses were performed at the Spang Microanalytical Laboratory, Ann Arbor, Mich. (c) All evaporations *in vacuo* were carried out with a Rinco rotating evaporator, Model 1007 4 IN.
(14) K. Freudenberg, H. Toepffer, and C. Anderson, *Ber.*, **61**, 1750 (1928).

water and alcohol. After being partially dried on the funnel by aspiration, the product was dried to constant weight *in vacuo* over phosphorus pentoxide; yield, 28.9 g. (67%).

Anal. Calcd. for $BaC_7H_{13}O_9S_2$: Ba, 15.97; monohydrate: Ba, 15.64. Found: Ba, 15.85.

Brucinium methyl α-D-glucopyranoside 2-sulfate. A solution of 12.2 g. (0.014 mole) of barium methyl 4,6-*O*-benzylidene-α-D-glucopyranoside monosulfate in 300 ml. of water was passed over an Amberlite IR-120 column (hydrogen-ion form). The combined acidic effluent and risings were heated at 60–65° for 30 min. then cooled and washed with two 100-ml. portions of ether to remove the liberated benzaldehyde. The solution was neutralized to *p*H 6.5 with alcoholic brucine. After removal of the alcohol *in vacuo*, the solution was washed with three 100-ml. portions of ether to remove the excess brucine. The solution was treated twice with 1-g. portions of Nuchar to remove the yellow color introduced with the brucine. After concentration to a sirup, about twenty volumes of acetone was added. A small amount of crystalline material was finally obtained. This proved to be brucinium sulfate. Sometimes, after a long period in the refrigerator, the desired product would crystallize out slowly. Frequently, however, it was necessary to obtain the first batch by a more devious route. The solution was concentrated to a thick sirup which was diluted with chloroform and absolute ethanol, the latter being used to keep the water from separating. When the total volume was about 500 ml., ether was added slowly, with heating and swirling until a permanent cloud was produced. Crystallization then occurred rapidly. The crystals were filtered off, washed with ether and dried *in vacuo* over phosphorus pentoxide. The yield of crude product was 12.0 g. (64.2%). This was dissolved in *ca.* 17 ml. of hot water and the solution diluted with 300 ml. of acetone. The solution was filtered then warmed and diluted with an additional 500 ml. of acetone. Scratching and refrigeration produced slow-growing rosettes of brucinium methyl α-D-glucopyranoside 2-sulfate (7.61 g.; 63.5% recovery). One further recrystallization gave the product in a very pure state. Its melting point was 213.5–214° dec. It had $[\alpha]_D^{25}$ +25.8° (*c* 3.344, in water).

Anal. Calcd. for $C_{30}H_{40}N_2O_{13}S$: C, 53.88; H, 6.03; N, 4.19; S, 4.80. Found: C, 53.89, 53.77; H, 5.98, 6.04; N, 4.32, 4.27; S, 4.76.

X-ray data (Ni filtered Cu K_α radiation): 14.66, 12.04, 10.61 (2), 7.314 (1, strongest), 6.932, 6.582 (5), 5.953 (2), 5.739, 5.343, 5.182, 4.952, 4.747, 4.407, 4.238 (4), 3.955, 3.770 (3), 3.664 (4), 3.570, 3.458, 3.336, 3.204.

Methyl 4,6-O-benzylidene-α-D-glycopyranoside 2,3-dinitrate was prepared by the method of Szabo and Szabo,[11] 15 g. of the glycoside yielding 12.2 g. (61.8%) of the crude dinitrate (m.p. 118.5–120°; lit.,[11] 124–125°).

Methyl 4,6-O-benzylidene-α-D-glucopyranoside 3-nitrate. The above compound (12.0 g.; 0.0323 mole) was treated with sodium nitrite (6 g.) and aqueous ethanol (60 ml. of ethanol +15 ml. of water) as directed by Honeyman and Morgan.[12] The yield was 7.72 g. (73.1% of ester having a melting point of 173.5–174.5° (lit.,[12] 174°).

Brucinium methyl α-D-glucopyranoside 3-nitrate 2-sulfate. To a solution of 3.27 g. (0.01 mole) of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 3-nitrate in 50 ml. of *N*,*N*-dimethylformamide was added 1.6 g. (0.01 mole) of pyridine–sulfur trioxide. The mixture was shaken until solution was complete (5 min.) and left at room temperature for 17 hr. The solvent was removed *in vacuo* and the resulting sirup taken up in 50 ml. of water. The odor of benzaldehyde was immediately noticeable. Therefore, advantage was taken of the acidic solution to remove the no longer necessary protecting group. The solution was kept at 50–60° for 20 min., then cooled and washed with three 25-ml. portions of ether to remove the benzaldehyde. It was then made basic to *p*H 10.0 with aqueous barium hydroxide. Carbon dioxide was bubbled in to *p*H 7.0 and the resulting suspension concentrated to a paste *in vacuo*, after the addition of some antifoaming agent. Upon resuspension in water, the material proved to be neutral; the inorganic salts and the antifoaming agent were removed by filtration. The solution was then passed over an Amberlite IR-120 column (hydrogen-ion form) and the combined effluent and rinsings neutralized to *p*H 5.8 with alcoholic brucine. The solution was treated with *ca.* 0.3 g. of Nuchar, filtered, and concentrated to a sirup. The sirup was taken up in 30 ml. of 95% ethanol and the solution made cloudy with ether.

It was warmed to clarity and placed in the refrigerator. Beautiful fluffy rosettes formed overnight; yield, 3.69 g. (51.8%). It had $[\alpha]_D^{20}$ + 21.1° (*c* 1.784, in water). A sample was recrystallized three times before being analyzed. It had m.p. 175–176.5° dec.

Anal. Calcd. for $C_{30}H_{39}N_3O_{15}S$: C, 50.49; H, 5.51; N, 5.89; S, 4.49. Found: C, 49.62, 49.66; H, 5.69, 5.66; N, 5.39; S, 4.14.

Brucinium methyl α-D-glucopyranoside 2-sulfate. A 0.714-g. (1.0 mmole) sample of brucinum methyl α-D-glucopyranoside 3-nitrate 2-sulfate dissolved in 100 ml. of 60% ethanol was shaken under hydrogen with 0.25 g. of palladium-on-charcoal catalyst[15] until uptake ceased. The catalyst was filtered off and the solution concentrated *in vacuo* to a crystalline mass, which was dissolved in *ca.* 0.6 ml. of warm water. The solution was diluted with 80 ml. of acetone and made cloudy with ether. After refrigeration, 0.491 g. (73.5%) of dihydrobrucinium methyl α-D-glucopyranoside 2-sulfate was obtained. Of this, 0.446 g. was dissolved in 20 ml. of water and the solution passed over an Amberlite IR-120 column (hydrogen-ion form). The combined effluent and rinsings were neutralized to *p*H 5.8 with alcoholic brucine. The solution was concentrated to a few drops *in vacuo*, and diluted with *ca.* 100 ml. of acetone. After refrigeration, 0.284 g. (63.8%) of brucinium methyl α-D-glucopyranoside 2-sulfate was obtained. It was proved to be identical with that prepared by sulfation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside by means of its x-ray diffraction pattern.

Demonstration of the uptake of hydrogen by brucinium methyl α-D-glucopyranoside 2-sulfate. A 0.334-g. (0.5 mmole) sample of brucinium methyl α-D-glucopyranoside 2-sulfate was reduced in 60% ethanol using the palladium-on-charcoal catalyst. The volume of hydrogen consumed was 11.4 ml. (S.T.P.) (0.51 mmole) proving that the uptake was on a mole for mole basis. A total of 0.165 g. (49.2%) of the dihydrobrucinium methyl α-D-glucopyranoside 2-sulfate was obtained. It had the same x-ray diffraction pattern as the material obtained from the reduction of brucinium methyl α-D-glucopyranoside 3-nitrate 2-sulfate. It was reconverted to the brucinium salt by ion exchange to the acid and neutralization with alcoholic brucine. The yield of "reconstructed" brucinium methyl α-D-glucopyranoside 2-sulfate was 0.149 g. (91%). It had the same x-ray diffraction pattern as the starting material before hydrogenation.

Nitration of the crude barium methyl 4,6-O-benzylidene-α-D-glucopyranoside sulfate. To a suspension of 4.30 g. (0.01 equiv.) of barium methyl 4,6-*O*-benzylidene-α-D-glucopyranoside sulfate in 15 ml. of acetic anhydride at −10°, was added over a 0.5 hr. period, a solution of 2.26 ml. of fuming nitric acid in 6 ml. of acetic anhydride cooled well below 0°. Thirty minutes after addition was complete, the solvents were removed *in vacuo* at less than 1 mm. and 5°. When only a frothy glass remained, the bath temperature was allowed to rise to 40°. The residue was taken up in 50 ml. of absolute ethanol which was then removed at less than 0° *in vacuo*. Attempts to crystallize a product from ethanol–ether mixtures failed. The solvents were removed and the remaining sirup taken up in 100 ml. of water. The solution was passed over an Amberlite IR-120 column (hydrogen-ion form) and the acid solution warmed to aid in the hydrolysis of benzylidene residue. After cooling, the solution was washed with two 35-ml. portions of ether to remove benzaldehyde, then neutralized to *p*H 6.1 with ethanolic

(15) E. C. Horning, *Org. Syntheses*, Coll. Vol. III, 685 (1955).

brucine. After discarding small batches of yellow gummy material obtained during the concentration of the solution, the residue was taken up in ethanol and the solution diluted with chloroform, then made cloudy with ether. A gelatinous precipitate, 1.66 g., was finally obtained and air dried. Some of this was subjected to hydrogenolysis followed by ion exchange and fresh brucine. The product thus obtained was found to be brucinium sulfate by its x-ray diffraction pattern and a sulfate test. Another sample was dissolved in a minimum of hot water, the solution diluted with ethanol, and finally made cloudy with ether. A crystalline product resulted. This was recrystallized for analysis. Its melting point was 197.5–200.5° dec. It gave negative sulfate and nitrate tests.

Anal. Found: C, 57.01, 56.97; H, 5.95, 6.01; N, 5.61; S, 6.04; O (by difference), 25.38.

These data indicate a molecular formula of $C_{50}H_{64}N_4O_{17}S_2$. Of the possible compounds it might be, brucinium methyl α-D-glucopyranoside disulfate comes closest to this: $C_{53}H_{66}N_4O_{20}S_2$, Calcd.: C, 55.68; H, 5.82; N, 4.90; S, 5.61. Per cent brucinium ion was determined by ion exchange[2] to the free acid followed by titration with standard base. As with the elemental analysis, the results were indicative of a disulfate but did not prove it: Calcd.: brucinium methylglucoside monosulfate, 59.1% brucinium ion; brucinium methyl glucoside disulfate, 69.2% brucinium ion. Found: 74% brucinium ion.

DEPARTMENT OF CHEMISTRY
SYRACUSE UNIVERSITY
SYRACUSE 10, N. Y.

Addition of Iodine Monochloride to Chlorotrifluoroethylene[1]

EUGENE R. BISSELL AND GRAHAM C. SHAW[2]

Received August 21, 1961

The recent publication of Haptschein, Braid, and Fainberg[3] on the addition of iodine monochloride to chlorotrifluoroethylene has prompted us to submit the following confirmatory and supplementary data from our own independent investigation. We have confirmed the formation of two isomers and have successfully separated them by vapor-liquid partition chromatography (VPC). The addition was carried out on a one-mole scale in a Parr low pressure hydrogenation apparatus and yielded 69% (based on iodine monochloride) of crude haloethanes consisting of roughly equal amounts of 1,2-dichloro-1-iodo-1,2,2-trifluoroethane (I) and 2,2-dichloro-1-iodo-1,1,2-trifluoroethane (II) with a small amount of 1,1,2-trichloro-1,2,2-trifluoroethane (III).

Pure I and II were obtained from the crude mixture by VPC in 1-ml. portions on an 18 mm. i.d. by 4-m. column of nonylphenoxy(polyethoxy)-ethanol on 42–60 mesh C-22 firebrick (25/100) at 100°. Helium at an inlet pressure of 24 p.s.i.g. was used as the carrier gas.

The identity of the individual isomers follows from the behavior of the corresponding dichlorotrifluoro-1-butenes derived from them by reaction with ethylene followed by dehydroiodination.[4] The butene derived from II [4,4-dichloro-3,3,4-trifluorobutene-1 (IV)] was recovered unchanged on treatment with zinc and isopropyl alcohol under conditions which converted that from I [3,4-dichloro-3,4,4-trifluorobutene-1 (V)] to 1,1,2 trifluorobutadiene.[5]

IV and V were purified by VPC on the nonylphenoxy(polyethoxy)ethanol column at 55°. V contained 1% of an unidentified impurity which was not separated on the nonylphenoxy(polyethoxy)ethanol column but was readily removed on a similar column of Zonyl E-91[6] at 55°. The molecular weight of IV as determined by PVT measurements was 180.0, that of V, 178.7 (Calcd. for $C_4H_3Cl_2F_3$, 179.0).

Physical properties of the two haloethanes and the two halobutenes are listed in Table I. The major infrared absorption bands for I in the vapor state were at 8.45, 9.10, 9.70, 11.50, 12.00, 12.50, 12.50, and 13.50 μ. Those for II were at 8.45, 8.60, 9.00, 9.85, 11.05, 11.80, and 13.3μ. Those for IV were at 7.10, 8.05, 8.40, 8.80, 9.25, 9.85, 10.20, 10.40, 11.05, 11.50, and 13.70 μ. Those for V were at 7.10, 8.20, 8.60, 9.20, 9.50, 9.80, 10.25, 10.45, 11.30, and 12.00 μ. A C=C stretching frequency was ob-

TABLE I

PHYSICAL PROPERTIES OF HALOETHANES AND HALOBUTENES

	I	II	IV	V
A[a]	7.5257	7.5089	7.5538	7.5394
B[a]	1751.8	1741.4	1632.0	1641.1
nbp. °C	103.9	103.1	76.0	79.1
$\Delta H_{vap.}$ cal./mole	7569	7506	7002	7045
Trouton ratio	20.1	19.9	20.0	20.0
$n^{25.2}D$	1.44816	1.44512	1.37382	1.37364
d_{23}	2.20	2.19	1.39	1.33
t_c/t_{CCl_4}[b]	3.12	2.69	0.95 (2.02)	0.73 (1.70)

[a] A and B are the constants for the vapor pressure equation $\log P_{(mm.\ Hg)} = A - B/T_{(°K)}$ in the range 300 to 800 mm. The vapor pressure curve and constants derived therefrom were obtained as previously described.[9] [b] Elution time ratios as defined in ref. 3 for a nonylphenoxy(polyethoxy)-ethanol column at 100° for I and II and at 55° for IV and V. Figures in parentheses are for the Zonyl E-91 column at 55°.

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) Present address, Utah Division, Thiokol Chemical Corp., Brigham City, Utah.

(3) M. Hauptschein, M. Braid, and A. H. Fainberg, *J. Am. Chem. Soc.*, **83**, 2495 (1961).

(4) J. D. La Zerte, D. A. Rausch, R. J. Kashar, J. D. Park, W. H. Pearlson, and J. R. Lacher, *J. Am. Chem. Soc.*, **78**, 5639 (1956).

(5) P. Tarrant and M. Lilyquist, *J. Am. Chem. Soc.*, **77**, 3640 (1955).

(6) E. I. du Pont de Nemours & Co., Inc., Organic Chemicals Department, Dyes and Chemicals Division, Wilmington 98 Del.