is this amount that is of particular interest in connection with the establishment of pressures suitable for the gaseous conduction of heat. From the approximate 40 cal. value for the molal heat of adsorption it may be seen that the forces holding the helium atoms are not of a much different magnitude than those existing in liquid helium.

It seems highly probable that when a calorimeter is suddenly cooled to temperatures below a degree, the approach to true adsorption equilibrium would occur very slowly and that the situation characterizing the condensed helium would resemble even more closely the conditions existing in liquid helium. In fact, considering the great change between 4.23 and 1.35°, we expect that the remaining pressure in a calorimeter at several tenths of a degree absolute will not differ greatly from that calculable for liquid helium. At the same time it is evident that an investigation extending over a day or two with the calorimeter often at, but not above, temperatures in the region between 1 and 2°K. may result in a serious cleanup of helium. It should be possible to avoid this by using enough helium to produce a layer two or three molecules deep if absorption does not occur as well as adsorption. However, the observations indicate that it is advantageous to heat a sample tube to temperatures of 4° or higher for occasional short periods to regenerate the conducting helium.

Summary

The adsorption of helium gas on nickel sulfate heptahydrate has been studied at the temperatures of liquid helium to obtain information relating to thermal equilibrium in calorimeters at these and at lower temperatures.

Equilibrium pressures have been measured for amounts estimated to form surface layers of the order of 1 to 2 molecules deep.

The heat of adsorption at 4.23°K. was found to be 131, 135, 137 and 148 cal./mole for the equilibrium pressures 1.12×10^{-3}, 7.1×10^{-4}, 5.8×10^{-4} and 1.6×10^{-4} cm., respectively.

When a calorimeter is cooled from 4.23 to 1.35° true adsorption equilibrium is not obtained within the time usually required for various magnetic and calorimetric experiments at these temperatures. In such a case the helium molecules adsorbed at the lower temperature are held more nearly like those of liquid helium.

BERKELEY, CALIF. RECEIVED DECEMBER 9, 1937

[CONTRIBUTION FROM THE CELLULOSE LABORATORY OF BOYCE THOMPSON INSTITUTE FOR PLANT RESEARCH]

The Unimolar Tosylation[1] of alpha- and beta-Methyl-*d*-glucosides

BY JACK COMPTON

The unimolar acylation of carbohydrate derivatives containing both primary and secondary hydroxyl groups leads to the preferential esterification of the former.[2] Among the secondary hydroxyl groups that may be present, the one adjacent to the carbonyl group, *i. e.*, position two in the aldose sugars, is usually the more reactive. In certain derivatives, the reactivity of the alpha secondary hydroxyl group is enhanced by the nature of the other substituents to equal that of the primary hydroxyl group. Thus, Lieser and Schweizer[2] found that the partial benzoylation of β-phenyl-*d*-glucoside in pyridine solution led to the formation of 6-benzoyl-β-phenyl-*d*-glucoside in high yield, whereas the partial benzoylation of both α- and β-methyl-*d*-glucoside resulted in the formation of 2,6-dibenzoyl-α-and β-methyl-*d*-glucosides, respectively. On the other hand, the reactivity of the alpha secondary hydroxyl group may be lowered by the nature of the other substituents in the molecule and by the conditions of acylation. Brigl and Mühlschlegel[3] thus have found that the benzoylation of glucose diethyl mercaptal with benzoyl chloride in aqueous alkaline solution led to the formation of 3,4,5,6-tetrabenzoylglucose diethyl mercaptal, but in pyridine solution a mixture of 2,3,4,5,6-pentabenzoylglucose diethyl mercaptal and 3,4,5,6-tetrabenzoylglucose diethyl mercaptal was obtained. The variable reactivity of the alpha secondary hydroxyl group shown in these cases is, perhaps, characteristic of the behavior of the secondary hydroxyl groups in other positions of the sugar molecule.

In the present investigation, a detailed quantitative study has been made of the unimolar tosyla-

(1) K. Hess and R. Pfleger, *Ann.*, **507**, 48 (1933).

(2) T. Lieser and R. Schweizer, *ibid.*, **519**, 271 (1935).

(3) P. Brigl and H. Mühlschlegel, *Ber.*, **63**, 1551 (1930).

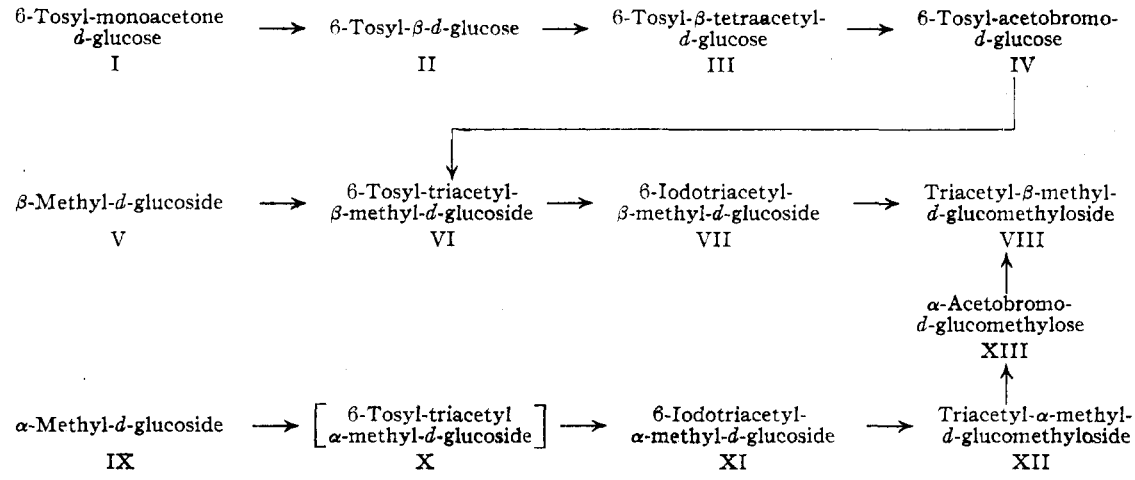

Fig. 1.—Interrelations

tion of α- and β-methyl-*d*-glucosides, to determine what effect the different spatial arrangements in the two substances would have upon the reactivity of the hydroxyl groups. Also, it was desirable in view of the work of Lieser and Schweizer[2] to determine what effect the nature of the acylating reagent would have in determining the order of reactivity of the various hydroxyl groups. The great relative stability of the tosyl esters and the ease with which the tosyl group in the primary position may be replaced by the iodo group to form the ω-iodo compound[4] makes this acylating reagent invaluable in this work.

The unimolar tosylation of β-methyl-*d*-glucoside (V) (Fig. 1) in pyridine solution followed by acetylation yielded 6-tosyl-triacetyl-β-methyl-*d*-glucoside (VI) in 41% yield. As a reference compound, (VI) was prepared from 6-tosyl-β-*d*-glucose (II), whose structure is definitely known from the parent substance 6-tosyl-monoacetone-*d*-glucose (I), by the series of reactions (I) to (IV) and (VI).

The unimolar tosylation of α-methyl-*d*-glucoside (IX) (Fig. 1) followed by acetylation yielded a mixture from which the 6-tosyl-triacetyl-α-methyl-*d*-glucoside (X) present could not be crystallized. However, treatment of the mixture with sodium iodide in acetone solution at 100° led to the formation of the easily crystallizable 6-iodotriacetyl-α-methyl-*d*-glucoside (XI) which may be removed quantitatively in 36% yield. As no reference compound of proven structure was available for final verification of the structure of 6-iodotriacetyl-α-methyl-*d*-glucoside, it was necessary to correlate the derivatives of the alpha series with those of beta by means of the following reactions: α-methyl-*d*-glucoside (IX) ⟶ 6-tosyl-triacetyl-α-methyl-*d*-glucoside (X) ⟶ 6-iodotriacetyl-α-methyl-*d*-glucoside (XI) ⟶ triacetyl-α-methyl-*d*-glucomethyloside (XII) ⟶ acetobromo-*d*-glucomethylose (XIII) ⟶ triacetyl-β-methyl-*d*-glucomethyloside (VIII). A reference sample of triacetyl-β-methyl-*d*-glucomethyloside was prepared by the reduction of 6-iodotriacetyl-β-methyl-*d*-glucoside (VII) of the beta series.

The physical constants and chemical analyses of triacetyl-β-methyl-*d*-glucomethyloside prepared from α-methyl-*d*-glucoside and β-methyl *d*-glucoside by way of the 6-tosyl esters prove the identity of the two substances and hence the course of the unimolar tosylation reaction in each case. It would appear probable, therefore, that the reactivity of the hydroxyl groups in α- and β-methyl-*d*-glucoside in pyridine solution is influenced by the nature of the acylating reagent.

Experimental

Crystalline 6-Tosyl-β-*d*-glucose (II).—6-Tosyl-monoacetone-*d*-glucose[5] (10 g.) was dissolved in 100 cc. of 70% acetic acid solution and allowed to stand at room temperature (26–30°) for seven days. The solution was then treated with charcoal, filtered, and concentrated under diminished pressure to a thick sirup from which the last traces of moisture and acetic acid were removed by repeatedly dissolving in absolute ethyl alcohol and concentrating under diminished pressure. The dry sirup was then dissolved in a large volume of hot ethyl acetate and petroleum ether (b. p. 30–50°) added until the solution was slightly turbid. After standing in the cold for several weeks the substance crystallized completely. The crystals were removed by filtration and washed with a mixture

(4) J. W. H. Oldham and J. K. Rutherford, THIS JOURNAL, **54**, 366 (1932).

(5) H. Ohle and L. v. Vargha, *Ber.*, **62**, 2430 (1929).

of ethyl acetate and petroleum ether (1:1): yield 6 g.; m. p. 132–133°; sp. rot.[6] +21.0° ⟶ +39.0° (four hours) (*c*, 2, H_2O). The substance is very soluble in water, alcohols and chloroform; slightly soluble in ethyl acetate; insoluble in ether and petroleum ether. *Anal.* Calcd. for $C_{13}H_{18}O_8S$: C, 46.68; H, 5.42. Found: C, 46.79; H, 5.50.

Preparation of 6-Tosyl-tetraacetyl-β-d-glucose (III).—Acetylation of crystalline 6-tosyl-β-d-glucose (11.5 g.) with acetic anhydride (35 cc.) in the presence of dry pyridine (80 cc.), according to the procedure of Ohle and Vargha,[5] yielded 6-tosyl-tetraacetyl-β-d-glucose. After one recrystallization of the dried material from dry pyridine, a melting point of 203–204° was obtained, unchanged by further recrystallization from this solvent: yield 12 g.; sp. rot. (25°) +23.7° (*c*, 3.665, $CHCl_3$).

6-Tosyl-acetobromo-d-glucose (IV).—6-Tosyl-tetraacetyl-β-d-glucose (3.4 g.) was dissolved in 10 cc. of glacial acetic acid saturated at 0° with dry hydrogen bromide, and allowed to stand two hours at room temperature. At the end of this time the hydrogen bromide and acetic acid were removed under diminished pressure at 40° by the addition of dry toluene followed by distillation under diminished pressure. Finally, the pure sirup was dissolved in a small volume of warm dry ether, treated with charcoal, and filtered. Upon cooling, the product separated in long crystalline needles, which were removed by filtration and washed with cold ether. Pure material was thus obtained after one recrystallization: yield 2.5 g.; m. p. 88–89°; sp. rot. +166.1° (*c*, 3.75, $CHCl_3$). *Anal.* Calcd. for $C_{19}H_{23}O_{10}SBr$: C, 43.58; H, 4.43; Br, 15.27. Found: C, 43.64; H, 4.69; Br, 15.28.

Preparation of 6-Tosyl-triacetyl-β-methyl-d-glucoside (VI) from 6-Tosyl-acetobromo-d-glucose (IV).—6-Tosyl-acetobromo-d-glucose (1.5 g.) was dissolved in 50 cc. of methyl alcohol and 4 g. of silver carbonate added. The mixture was heated, with shaking, on the boiling water-bath for forty-five minutes, after which it was treated with charcoal and filtered. Upon cooling the clear filtrate, the product separated in fine white needles: yield 1.2 g.; m. p. 167–168°. After one further recrystallization from methyl alcohol, a melting point of 170–171° was obtained, unchanged by further recrystallization; sp. rot. +7.2° (*c*, 3.75, $CHCl_3$). *Anal.* Calcd. for $C_{20}H_{26}O_{11}S$: C, 50.61; H, 5.52; OCH_3, 6.53. Found: C, 50.82; H, 5.49; OCH_3, 6.44.

Employing conditions similar to those given above, Ohle and Vargha[5] obtained VI with melting point 164°; however, Helferich, Bredereck and Schneidmüller[7] upon tosylating 2,3,4-triacetyl-β-methylglucoside in pyridine solution obtained (VI) with melting point 171°.

Unimolar Tosylation of β-Methyl-d-glucoside (V) Followed by Acetylation to Yield 6-Tosyl-triacetyl-β-methyl-d-glucoside (VI).—Five grams of β-methyl-d-glucoside was dissolved in 50 cc. of dry pyridine and to the ice-cold solution 5.39 g. (1.1 mol.) of tosyl chloride dissolved in 50 cc. of dry pyridine was added over a period of fifteen minutes with rapid stirring. After standing for one hour at 0°, the mixture was removed from the ice-bath and allowed to stand for twenty-four hours at room temperature. At the end of this time the solution was again cooled to 0° and 40 cc. of acetic anhydride added, with rapid stirring. The mixture was then allowed to stand for one hour at 0° and overnight at room temperature. At the end of the acetylation period the solution was cooled to 0° in an ice-bath and 10 cc. of water added with vigorous stirring over a period of thirty minutes. The solution was then diluted with chloroform and the chloroform extract washed with ice water, ice-cold 10% sulfuric acid solution, saturated sodium bicarbonate solution and finally with ice water. After drying over anhydrous sodium sulfate the extract was concentrated under diminished pressure at 40° to a thick sirup which crystallized after the addition of a small amount of ethyl alcohol; yield, 5.5 g. contaminated with a small amount of tetraacetyl-β-methyl-d-glucoside. After the third recrystallization from absolute ethyl alcohol, a pure product was obtained; m. p. 169–170°; yield 5.0 g. A mixed melting point of this material with (VI) obtained from (IV) showed no depression; sp. rot. (30°) +7.4° (*c*, 3.654, $CHCl_3$). *Anal.* Calcd. for $C_{20}H_{26}O_{11}S$: C, 50.61; H, 5.52; OCH_3, 6.53. Found: C, 50.88; H, 5.72; OCH_3, 6.48.

The yield of (VI) indicated that approximately 41% of the available β-methyl-d-glucoside was preferentially esterfied in the primary position, when treated with one mole of tosyl chloride.

Preparation of 6-Iodotriacetyl-β-methyl-d-glucoside (VII).—The procedure of Oldham[8] for the preparation of (VII) from 6-nitrotriacetyl-β-methyl-d-glucoside was employed successfully, with slight modification, in the conversion of (VI) into (VII).

6-Tosyl-triacetyl-β-methyl-d-glucoside (1.5 g.) was dissolved in 10 cc. of C. P. acetone and to the solution 1.5 g. of sodium iodide dissolved in 10 cc. of acetone was added. The mixture was heated in a sealed tube at 100° for one and one-half hours, cooled, the tube opened and the filtered solution concentrated under diminished pressure to dryness at 40°. The solid was then dissolved in a mixture of chloroform and water, the chloroform extract separated and washed with water, dilute sodium thiosulfate solution, and finally with water. After drying over anhydrous sodium sulfate the chloroform extract was concentrated under diminished pressure to a crystalline solid. One recrystallization from absolute ethyl alcohol gave a pure product; m. p. 114–115°; yield, 1.0 g.; sp. rot. +2.4° (*c*, 3.755, $CHCl_3$). Oldham obtained a product; m. p. 111–112.5°; sp. rot. +0.9° ($CHCl_3$). *Anal.* Calcd. for $C_{13}H_{19}O_8I$: C, 36.27; H, 4.45; OCH_3, 7.21. Found: C, 36.47; H, 4.78; OCH_3, 7.15.

Preparation of Triacetyl-β-methyl-d-glucomethyloside (VIII) from 6-Iodotriacetyl-β-methyl-d-glucoside (VII).—With slight modification, (VIII) was prepared from (VII) by the procedure of Micheel[9] for the preparation of (VIII) from 6-bromotriacetyl-β-methyl-d-glucoside.

6-Iodotriacetyl-β-methyl-d-glucoside (1.38 g.) was dissolved in 14 cc. of 50% acetic acid solution containing a trace of chloroplatinic acid and heated on a boiling water-bath with vigorous stirring during the portion-wise addition of 3.5 g. of zinc dust over a period of thirty minutes.

(6) All specific relations herein recorded were determined with the D-line of sodium light at 26°, unless otherwise specified.

(7) B. Helferich, H. Bredereck and A. Schneidmüller, *Ann.*, **458**, 111 (1927).

(8) J. W. H. Oldham, *J. Chem. Soc.*, 2840 (1925).

(9) F. Micheel, *Ber.*, **63**, 347 (1930).

At the end of this time the hot solution was filtered and the zinc residue thoroughly washed with acetic acid. The filtrate was concentrated under diminished pressure at 40° to a solid mass which was then dissolved in a mixture of ether and water. The water layer was extracted thoroughly with ether and the combined ether layers washed with water, saturated sodium bicarbonate solution and finally with water. After drying over anhydrous sodium sulfate the filtered solution was concentrated under diminished pressure to a sirup which crystallized upon standing a short time. Pure material was obtained after one recrystallization from methyl alcohol; m. p. 103–104°; yield 0.9 g.; sp. rot. −12.3° (*c*, 3.7375, $CHCl_3$). The product obtained by Micheel melted at 100°. *Anal.* Calcd. for $C_{13}H_{20}O_8$; C, 51.28; H, 6.62; OCH_3, 10.19. Found: C, 51.06; H, 6.79; OCH_3, 10.28.

Unimolar Tosylation of α-Methyl-*d*-glucoside (IX) Followed by Acetylation to Yield Sirupy 6-Tosyl-triacetyl-α-methyl-*d*-glucoside (X) and its Conversion to Crystalline 6-Iodotriacetyl-α-methyl-*d*-glucoside (XI).—Ten grams of α-methyl-*d*-glucoside was dissolved in 100 cc. of dry pyridine and 10.62 g. (1.1 mol) of tosyl chloride dissolved in 100 cc. of dry pyridine was added over a period of thirty minutes with good stirring after cooling both solutions to 0°. The mixture was then treated in exactly the same manner as in the unimolar tosylation–acetylation procedure described in the preparation of (VI); yield of sirupy material 22 g. Despite all attempts at crystallization it was impossible to separate (X) from the mixture. As shown below, this substance was present to the extent of 36%, but the preponderance of impurities prevented its crystallization.

Sirupy (X) (22 g.) was dissolved in 75 cc. of acetone and 22 g. of sodium iodide dissolved in 75 cc. of acetone added. The mixture was heated in a sealed tube at 100° for one and one-half hours, after which the product was purified and isolated in the manner described for the preparation of (VII) from (VI). After one recrystallization from methyl alcohol, pure material was obtained; m. p. 149–150°; yield 9.03 g.; sp. rot. +113.8° (*c*, 3.7425, $CHCl_3$).

Helferich and Himmen,[10] by a similar procedure obtained (XI) from crystalline (X), with melting point 150–151° (corr.); sp. rot. +116.1° ($CHCl_3$).

The ease with which (XI) crystallizes from mixtures was especially valuable in the present case since a direct means was thus afforded for the calculation of the amount of (X) first formed. In this manner it was possible to determine that in the unimolar tosylation of α-methyl-*d*-glucoside 36.0% of the material was preferentially esterified in the primary position.

Preparation of Triacetyl-α-methyl-*d*-glucomethyloside (XII) from 6-Iodotriacetyl-α-methyl-*d*-glucoside (XI).—The reduction of (XI) to yield (XII) was carried out essentially according to the procedure of Helferich, Klein, and Schaefer[11] for the preparation of (XII) from 6-bromotriacetyl-α-methyl-*d*-glucoside.

To a solution of 35 cc. of 75% acetic acid containing 5.6 g. of 6-iodotriacetyl-α-methyl-*d*-glucoside and a trace of chloroplatinic acid heated on a boiling water-bath, 12.5 g. of zinc dust was added portion-wise with vigorous stirring over a period of thirty minutes. The procedure described above for the preparation of (VIII) from (VII) was followed except that in the present case the sirupy product was dissolved in boiling petroleum ether (b. p. 30–50°) and allowed to stand in the cold overnight. The product separated in long prismatic clusters which were removed by filtration and washed with petroleum ether; yield 2.5 g. After the second recrystallization from petroleum ether, pure material was obtained; m. p. 77–78°; sp. rot. (24°), +153.6° (*c*, 3.8075, $CHCl_3$).

Preparation of α-Acetobromo-*d*-glucomethylose (XIII) from Triacetyl-α-methyl-*d*-glucomethyloside (XII).—With modifications, (XIII) was prepared from (XII) according to the procedure of Micheel[9] for the preparation of (XIII) from triacetyl-β-methyl-*d*-glucomethyloside.

Two grams of triacetyl-α-methyl-*d*-glucomethyloside was dissolved, at room temperature, in 5 cc. of glacial acetic acid saturated at 0° with dry hydrogen bromide. After fifteen minutes the acetobromo compound began to separate in fine crystalline needles and after a further fifteen minutes had set to a solid mass. The product was then taken up in 100 cc. of chloroform and rapidly washed with ice water. After the third washing the extract was dried over anhydrous sodium sulfate, filtered, and concentrated under diminished pressure at 40° to a thick sirup which crystallized upon standing a short time. After one recrystallization from benzene, a melting point of 150–152° was obtained, unchanged by further recrystallizations: yield 1.2 g.; sp. rot. +246.6° (*c*, 3.892, $CHCl_3$). *Anal.* Calcd. for $C_{12}H_{17}O_7Br$: C, 40.76; H, 4.85; Br, 22.62. Found: C, 40.56; H, 5.00; Br, 22.58.

Micheel reported a melting point of 135–136°; sp. rot. +228.4° ($CHCl_3$) for (XIII). The analyses obtained in the present case, however, indicate a very high degree of purity.

Preparation of Triacetyl-β-methyl-*d*-glucomethyloside (VIII) from α-Acetobromo-*d*-glucomethylose (XIII).—α-Acetobromo-*d*-glucomethylose (1.7 g.) was dissolved in 50 cc. of methyl alcohol and to the solution 5 g. of silver carbonate was added. After refluxing on the water-bath for one hour, the mixture was treated with charcoal, filtered, and the clear filtrate concentrated under diminished pressure at 40° to a sirup which soon crystallized. After one recrystallization from methyl alcohol, a pure product was obtained; m. p. 103–104°; yield 1.18 g.; sp. rot. −12.6° (*c*, 3.785, $CHCl_3$). *Anal.* Calcd. for $C_{13}H_{20}O_8$: C, 51.28; H, 6.62; OCH_3, 10.19. Found: C, 51.12; H, 6.75; OCH_3, 10.13.

A mixed melting point of the material thus obtained with (VIII) obtained from (VII) showed no depression. From the rotations, melting points, mixed melting point and analyses there remains no doubt that the two substances are identical.

The author wishes to express his appreciation to Miss Jeanne Thompson for the micro-analyses reported in this work.

Summary

1. The unimolar tosylation of α- and β-methyl-*d*-glucosides in pyridine solution with tosyl chloride, followed by acetylation, results in the

(10) B. Helferich and E. Himmen, *Ber.*, **61**, 1825 (1928).
(11) B. Helferich, W. Klein and W. Schaefer, *ibid.*, **59**, 79 (1926).

formation of 6-tosyl-triacetyl-α-methyl-*d*-glucoside in 36% yield and 6-tosyl-triacetyl-β-methyl-*d*-glucoside in 41% yield, respectively. Employing the acylation conditions specified, the differences in spatial arrangement of these isomeric compounds nas little or no effect on the order of reactivity of the various hydroxyl groups.

2. The structure of 6-tosyl-triacetyl-β-methyl-*d*-glucoside, obtained by the unimolar tosylation of β-methyl-*d*-glucoside followed by acetylation, is proven by its identity with 6-tosyl-triacetyl-β-methyl-*d*-glucoside derived from 6-tosyl-monoacetone-*d*-glucose.

3. The structure of 6-tosyl-triacetyl-α-methyl-*d*-glucoside obtained by the unimolar tosylation–acetylation of α-methyl-*d*-glucoside in pyridine solution is proven by the following reactions: 6-tosyl-triacetyl-α-methyl-*d*-glucoside ⟶ 6-iodo-triacetyl-α-methyl-*d*-glucoside ⟶ triacetyl-α-methyl-*d*-glucomethyloside ⟶ acetobromo-*d*-glucomethylose ⟶ triacetyl-β-methyl-*d*-glucomethyloside. The triacetyl-β-methyl-*d*-glucomethyloside obtained in this manner was found to be identical with the reduction product of 6-iodo-triacetyl-β-methyl-*d*-glucoside obtained from 6-tosyl-triacetyl-β-methyl-*d*-glucoside, thus correlating the derivatives of the alpha and beta series.

4. In view of the results of Lieser and Schweizer on the partial benzoylation of α- and β-methyl-*d*-glucosides, the suggestion is made that the order of the reactivity of the hydroxyl groups in these compounds may be influenced by the nature of the acylating reagent.

YONKERS, NEW YORK RECEIVED OCTOBER 28, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

Sulfonic Acid Esters of the Phenylphenols

BY STEWART E. HAZLET

Recently some sulfonic acid esters of the phenylphenols were reported[1] and their characteristics listed. Some of these were rather low melting compounds and not particularly suitable as derivatives for the identification of the phenols. The *p*-bromo- and the *o*-, *m*- and *p*-nitrobenzenesulfonates of the three isomeric phenylphenols have now been characterized and the results are summarized in Tables I, II, III and IV.

TABLE I

ESTERS OF *p*-BROMOBENZENESULFONIC ACID

Starting material	Solvent	Yield, %	M. p., °C.	Formula	Sulfur analyses, % Calcd.	Found
o-Phenylphenol	Methanol	69	69–70	$C_{18}H_{13}O_3BrS$	8.24	8.36
m-Phenylphenol	Dil. alcohol	28	102.5–103.5	$C_{18}H_{13}O_3BrS$	8.24	8.46
p-Phenylphenol	Alcohol	90	185–186	$C_{18}H_{13}O_3BrS$	8.24	8.34

TABLE II

ESTERS OF *o*-NITROBENZENESULFONIC ACID

Starting material	Solvent	Yield, %	M. p., °C.	Formula	Sulfur analyses, % Calcd.	Found
o-Phenylphenol	Dil. alcohol	89	72–73	$C_{18}H_{13}O_5NS$	9.03	9.05
m-Phenylphenol	Methanol	60	69–70	$C_{18}H_{13}O_5NS$	9.03	9.01
p-Phenylphenol	Alcohol	Quant.	138–139	$C_{18}H_{13}O_5NS$	9.03	9.1

TABLE III

ESTERS OF *m*-NITROBENZENESULFONIC ACID

Starting material	Solvent	Yield, %	M. p., °C.	Formula	Sulfur analyses, % Calcd.	Found
o-Phenylphenol	Alcohol	77	130–131	$C_{18}H_{13}O_5NS$	9.03	9.17
m-Phenylphenol	Alcohol	38	111–112	$C_{18}H_{13}O_5NS$	9.03	9.34
p-Phenylphenol	Alcohol	85	143–144	$C_{18}H_{13}O_5NS$	9.03	9.17

The method of preparation in each instance was the same as that previously used.[1] The phenol was dissolved in pyridine and treated with 1.1 mols of the necessary acid chloride. Yields re-

(1) Hazlet, THIS JOURNAL, 59, 287 (1937).