part of the sublimation tube; yield, 1.23 g. (65%); m. p. 203–208°. In one run 0.6 g. (78%) of sublimed product was obtained from 0.81 g. of the cyclic ketone. A sample of the **hydrocarbon** (V) crystallized from benzene in yellow rhombic plates; m. p. 209–213°. It dissolves slowly in concentrated sulfuric acid to give an emerald green solution.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.2; H, 5.7. Found: C, 93.7; H, 5.7.

The **picrate** crystallized from benzene in dark-red needles; m. p. 177.5–178°.

Anal. Calcd. for $C_{22}H_{16}\cdot C_6H_3N_3O_7$: N, 8.3. Found: N, 8.3.

The unrecrystallized hydrocarbon (1.23 g.; m. p. 203–208°) and 0.2 g. of palladium–charcoal catalyst[7] were heated in a nitrogen atmosphere at 310–330°. After twenty minutes the material which had sublimed up on the sides of the tube was washed down with a little benzene, the benzene was evaporated and the heating continued for ten minutes. The product was then sublimed directly from the catalyst at 0.01 mm.; the bright orange sublimate weighed 0.97 g. and melted at 240–246.5° (vac.). A solution of 1.2 g. of such sublimed product in benzene was passed through a short tower of alumina and the solution was concentrated under reduced pressure; addition of a little petroleum ether caused the **4′,5-dimethylene-3,4-benzpyrene** to separate as bright orange platelets; yield, 0.78 g.; m. p. 251–252° (255–256° cor.) in an evacuated tube; the melting point in air is somewhat lower because of oxidation. From the filtrate an additional 0.29 g. of practically pure hydrocarbon was isolated. The hydrocarbon is very slightly soluble in cold alcohol and ether, slightly soluble in cold benzene and only moderately soluble in boiling benzene. It gives a violet color with concentrated sulfuric acid; in a few minutes the color changes to a beautiful magenta (yellow-orange fluorescence).

Anal. Calcd. for $C_{22}H_{14}$: C, 94.9; H, 5.1. Found: C, 94.8, 95.23; H, 4.9, 5.0.

The **picrate** crystallized from benzene in almost black needles; m. p. 177–177.5°.

Anal. Calcd. for $C_{22}H_{14}\cdot C_6H_3N_3O_7$: N, 8.3. Found: N, 8.4.

Conversion of 1-Ketotetrahydrocholanthrene (VII) to Cholanthrene.—One-half gram of the ketone[8] was reduced by aluminum isopropoxide in the manner described. The crude **1-hydroxytetrahydrocholanthrene** was recrystallized from benzene, from which it separated in fine colorless rhombic platelets and needles. The first crop weighed 0.32 g. and melted at 146.5–147.5°; this was suitable for the next step. A sample after another recrystallization melted at 150–150.5°.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.6; H, 6.6. Found: C, 87.6; H, 6.8.

Dehydration of 100 mg. of the secondary alcohol by heating it gradually to 240° at 5 mm. and after cessation of frothing evaporatively distilling at 0.05 mm. gave 80 mg. of product melting at 136–137°. When this was dehydrogenated with palladium on charcoal in the manner described, there was obtained 51 mg. of practically pure cholanthrene.

Summary

The polycyclic hydrocarbon 4′,5-dimethylene-3,4-benzpyrene which possesses the basic structures of both cholanthrene and 3,4-benzpyrene has been synthesized from 4′-ketotetrahydro-3,4-benzpyrene and its absorption spectrum has been measured.

The preparation of 1′,2′-dihydro-3,4-benzpyrene is described. The two new polycyclic hydrocarbons are being tested for carcinogenic activity.

ANN ARBOR, MICHIGAN RECEIVED MARCH 4, 1941

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[7] Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

[8] Bachmann, *J. Org. Chem.*, **3**, 434 (1938).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Mesylated Cellulose and Derivatives[1]

BY M. L. WOLFROM, JOHN C. SOWDEN[2] AND E. A. METCALF[2]

A long-known process for the surface alteration of cellulose fibers to make them resistant or "immune" to direct dyes consists in the treatment of alkali cellulose with *p*-toluenesulfonyl chloride (tosyl chloride).[3] The scientific aspects of this process formed the subject of investigations carried out in the laboratories of G. Kita in Japan.[4] The tosylation of cellulose with *p*-toluenesulfonyl chloride in pyridine solution was studied carefully by Hess and Ljubitsch[5] and more recently by Bernoulli and Stauffer.[6]

The tosyl esters of cellulose are of interest because their chemical reactivity resembles that of a

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[1] Presented before the Division of Cellulose Chemistry at the 101st Meeting of the American Chemical Society, St. Louis, Missouri, April 9, 1941.

[2] Du Pont Cellulose Research Fellow.

[3] German Patents: Agfa, 200,334 (1907); Casella, 346,883 1919); Textilwerke Horn, 396,926 (1922); Chem. Werke vorm. Sandoz, 545,323 (1929), 521,121 (1929).

[4] I. Sakurada and T. Nakashima, *Sci. Papers Inst. Phys. chem. Research* (Tokyo), **6**, 214 (1927); *C. A.*, **22**, 684 (1928); *Bull. Inst. Phys. Chem. Research* (Tokyo), **8**, 272 (1929); *C. A.*, **23**, 3572 (1929).

[5] K. Hess and N. Ljubitsch, *Ann.*, **507**, 62 (1933).

[6] A. L. Bernoulli and H. Stauffer, *Helv. Chim. Acta*, **23**, 627 (1940).

halide rather than that of a true ester of an oxygen acid.[7] In monosaccharide derivatives, the tosyl group on the terminal primary alcohol function is replaceable by iodine and by the amino group. Certain difficulties are inherent in the application of the pyridine tosylation procedure to cellulose. The cellulose reacts slowly and heterogeneously and must be previously activated. At 70° considerable amounts of chlorine and nitrogen are introduced but Hess and Ljubitsch[5] were able to introduce two tosyl groups per anhydroglucose unit by operating at 15–20° for four days, obtaining a product that contained only slight amounts of chlorine and nitrogen. The introduction of chlorine, which takes place with a decrease in sulfur content, may be due to tosyl replacement by chlorine, a reaction demonstrated by Hess and Stenzel[8] for positions four and six of the tetra-tosylated methylglucopyranosides. Bernoulli and Stauffer[6] suggest that the chlorine may be mainly on the reducing carbon of degraded cellulose chains. The binding of nitrogen may be due to pyridinium salt formation, particularly if the halogen is an acetal halogen on carbon one.

The direct replacement of tosyl by ammonia to produce cellulosic products with a lowered sulfur content and some content of nitrogen has been accomplished by Karrer and Wehrli[9] and by Sakurada[10] with tosylated cellulose of low tosyl content. Hess and Ljubitsch[5] demonstrated that their ditosyl cellulose on reaction with ammonia underwent partial tosyl replacement with the production of products containing less than 2% of nitrogen.

Esterification with methanesulfonyl chloride has been employed recently with monosaccharides,[11] wherein it was observed that the mesyl (methanesulfonyl) group was introduced somewhat more readily than the tosyl group. The resulting mesyl esters were found to be more reactive than the tosyl esters. Thus, iodine replacement by the action of sodium iodide in acetone was not confined exclusively to the 6-mesyl group but also took place readily with a substituted 4-mesyl glucose. Moreover, the 6-mesyl group could be replaced readily by acetyl by the action of potassium acetate, or by amino by reaction with liquid ammonia.

It was considered of interest to apply to cellulose these mesylation procedures in the hope that this apparently more reactive group might exhibit properties preferable to those of the tosyl group, particularly with respect to the problem of obtaining an amino-substituted cellulose. Such was not found to be the case, and the mesylation results obtained with cellulose paralleled the findings of Hess and Ljubitsch[5] with tosylated cellulose.

High viscosity cotton linters, activated by mercerization or by regeneration from a cellulose acetate, reacted heterogeneously and slowly at room temperature with mesyl chloride and pyridine. Figure 1 is a plot of the rate of increase in sulfur content of the mercerized linters, the lower curve representing the data obtained with the theoretical (three moles) of mesyl chloride and the upper curve that obtained with a considerable excess of mesyl chloride. As with tosylation, the reaction proceeds to a product approximating a dimesyl derivative containing negligible amounts of chlorine and nitrogen. The curve rises initially in a continuous manner and no break at the monomesylation stage can be noted in this heterogeneous reaction. With longer periods of time, the sulfur content decreases.

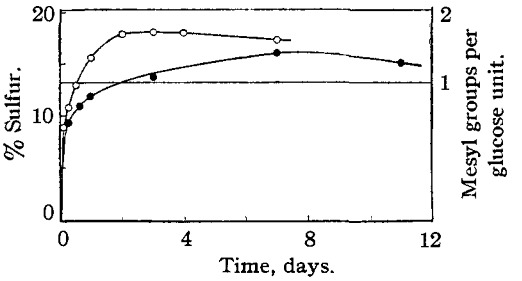

Fig. 1.—Rate of mesylation of mercerized cotton linters in pyridine at room temperature: ○, 6 moles of mesyl chloride per glucose unit; ●, 3 moles of mesyl chloride per glucose unit.

In order to obtain conditions of homogeneous reaction, a pyridine-soluble modified cellulose acetate (1.7 acetate groups per anhydroglucose unit) was subjected to mesylation in pyridine solution and one mesyl group (per glucose unit) was introduced readily. On reaction with pyridine hydrochloride in pyridine solution at 80°, this product underwent change to produce a substance containing a lowered sulfur content and appreciable amounts of chlorine.

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(7) F. Ullmann and G. Nádai, *Ber.*, **41**, 1870 (1908).

(8) K. Hess and H. Stenzel, *ibid.*, **68**, 981 (1935).

(9) P. Karrer and W. Wehrli, *Helv. Chim. Acta*, **9**, 591 (1926); *Z. angew. Chem.*, **39**, 1509 (1926).

(10) I. Sakurada, *Bull. Inst. Phys. Chem. Research* (Tokyo), **8**, 265 (1929); *C. A.*, **23**, 3572 (1929).

(11) B. Helferich and A. Gnüchtel, *Ber.*, **71B**, 712 (1938); B. Helferich and R. Mittag, *ibid.*, **71B**, 1585 (1938).

Cramer and Purves[12] recently have reported experiments concerned with the successful introduction of iodine into the cellulose molecule. The above mixed acetate, methanesulfonate (one mesyl group per glucose unit) reacted with sodium iodide to yield a product that was sulfur-free and contained 0.4 atom of iodine (18% iodine) per glucose unit, assuming no acetate loss. This was the maximum amount of iodine that could be introduced, although a variety of conditions were used. The fate of the 0.6 mesyl group (per glucose unit) not replaced by iodine is not clear. The temperature of the reaction was high and pyrolysis with loss of iodine may have occurred. Fractionation is not excluded, as the yield was low, and the product possibly may have resulted from a fraction of the mesylated cellulose acetate that contained originally only 0.4 mesyl group (per glucose unit).

The action of aqueous ammonia on mesylated celluloses or on the above mixed acetate, methanesulfonate of cellulose, led to partial replacement of the mesyl groups to yield products that contained appreciable amounts of sulfur (3 to 6%) and nitrogen (0.5 to 4%).

Experimental

Materials.—The cellulose used was high viscosity, bleached cotton linters.[13] The cellulose acetate[14] used contained 31.5% acetyl, as determined by the procedure of Malm and Clarke,[15] which corresponds to 1.7 acetate groups per glucose unit. The methanesulfonyl chloride (mesyl chloride) was prepared according to the procedure of Douglass and Johnson.[16] It is to be noted that the chlorination step in the procedure of Johnson and Sprague[17] may lead to violent explosions and this method is not recommended. Pyridine of high quality was dried by refluxing over barium oxide, distilled and stored over Drierite.

Mesylation of Cellulose.—Cotton linters (10 g., 1 mol) were mercerized with 220 cc. of 18% sodium hydroxide for one hour at room temperature. The alkali was removed by washing profusely with water and the water displaced with dry pyridine. The cellulose was suspended in 250 cc. of dry pyridine and the suspension cooled to 0°. To this was added, with vigorous shaking, mesyl chloride (42.4 g., 6 mols), previously cooled to 0°. A slight exothermic reaction took place on mixing. The reaction was allowed to proceed at room temperature for forty-eight hours. The cellulose did not dissolve and the color of the liquid gradually deepened to a reddish-brown. At the end of this period the reaction product was removed by filtration and washed with hot water until the washings were colorless. The water was displaced with acetone and the product, a light tan solid, was air-dried overnight; yield 10 g.

Anal.[18] Calcd. for $C_6H_8O_5(CH_3SO_2)_2$: S, 20.14. Found: S, 17.9 (1.6 mesyl groups per glucose unit); N, absent; Cl, trace.

Mesylation at higher temperatures produced darker products. Thus, in one experiment the conditions used were as described above except that the reaction was carried out at a temperature of 45–50° for twenty-four hours and a nitrogen atmosphere was maintained.

Anal. S, 13.0 (1.0 mesyl group per glucose unit).

Mercerized cotton linters were mesylated at room temperature for different periods of time as described above and the variation of sulfur content with time of reaction is plotted in the upper curve of Fig. 1. A reaction which was allowed to run for seventeen days at room temperature showed a sulfur content of 8.0% (0.5 mesyl group per glucose unit). The lower curve of Fig. 1 shows the variation in sulfur content with time of reaction with a ratio of three moles of mesyl chloride per mole of cellulose.

A regenerated cellulose sample, prepared by saponification of the cellulose acetate (15 g.) (see section on materials) according to the procedure of Malm and Clarke,[15] was mesylated at room temperature as described above (6 moles of mesyl chloride per mole of cellulose) and the reaction product obtained (four days reaction time) was purified by dissolving in boiling acetonylacetone (400 cc.), cooling and pouring slowly with stirring into 2 liters of water. The colloidal solution thus formed was coagulated by adding a small amount of electrolyte and passing through a 110-volt alternating current until the mixture was heated just short of boiling. The product was then removed by filtration, washed and dried at 60° under reduced pressure. A creamy white powder was obtained; yield 13.9 g.

Anal. S, 18.3 (1.7 mesyl groups per glucose unit).

Mesyl Cellulose Acetate.—Ten grams of cellulose acetate (1.72 acetate groups per glucose unit), previously dried for five hours at 75° under reduced pressure, was dissolved in dry pyridine (200 cc.), mesyl chloride (6 cc.) added and the solution maintained at room temperature for four days. The reaction mixture was then diluted with water (5 cc.) and acetone (200 cc.) and the reaction product precipitated by the drop-wise addition, with stirring, of 400 cc. of 50% acetone. The product was removed by filtration, washed with water and 75% acetone and dried at 50° under reduced pressure; yield 12.6 g. The product was a practically white powder that was readily soluble in acetone and pyridine.

Anal. S, 10.5 (1.72 acetate and 1.03 mesyl groups per glucose unit); N, absent; Cl, trace.

Saponification of the above product (5.0 g.) according to the procedure of Malm and Clarke[15] yielded a creamy-white product (2.7 g.).

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(12) F. B. Cramer and C. B. Purves, This Journal, **61**, 3458 (1939).

(13) Furnished through the courtesy of the Hercules Powder Company, Wilmington, Delaware.

(14) Furnished through the courtesy of E. I. du Pont de Nemours and Company, Waynesboro, Virginia.

(15) C. J. Malm and H. T. Clarke, This Journal, **51**, 274 (1929).

(16) I. B. Douglass and T. B. Johnson, *ibid.*, **60**, 1486 (1938).

(17) T. B. Johnson and J. M. Sprague, *ibid.*, **58**, 1348 (1936).

(18) All analyses were performed on samples dried over phosphorus pentoxide under reduced pressure and at elevated temperatures, or on samples corrected for determined moisture content.

Anal. S, 8.0 (0.5 mesyl group per glucose unit).

Action of Pyridine Hydrochloride on Mesyl Cellulose Acetate.—Mesyl cellulose acetate (3.5 g., 1.0 mesyl and 1.7 acetate groups per glucose unit) was dissolved in dry pyridine (90 cc.), pyridine hydrochloride (*ca.* 4 g.) added, and the solution heated for five hours at 80–85°. The reddish-brown solution then was added drop-wise with stirring to 1.5 liters of water. The filtered product was purified by pouring its solution in warm acetonylacetone (100 cc.) into 1.5 liters of water. To the colloidal dispersion thus formed was added a little electrolyte and on passing an alternating 110-volt current through the solution until it was heated to boiling, the precipitate was coagulated; yield 3.5 g. of a light tan powder.

Anal. S, 9.0; Cl, 3.3; N, trace (1.7 acetate, 0.9 mesyl groups and 0.3 chlorine atoms per glucose unit).

Similar products containing sulfur and chlorine but of lighter color and easier filterability may be obtained directly by mesylation of the cellulose acetate in pyridine at 90°.

Mesyl Iodocellulose Acetate.—Five grams of mesyl cellulose acetate (1.7 acetate and 1.0 mesyl groups per glucose unit) was refluxed for one hour with acetonylacetone (70 cc.) and sodium iodide (10 g.). The cooled solution was filtered from a finely divided precipitate of sodium methanesulfonate and the filtrate poured slowly with stirring into 1 liter of water and the precipitate removed by filtration. The product was purified by solution in acetonylacetone, treatment with decolorizing charcoal, and precipitation by pouring into an excess of water; yield 1.2 g. The product was a very light tan powder that evolved iodine on heating in a test-tube over a Bunsen flame.

Anal. S, absent; I, 17.8 (0.4 iodine atom per glucose unit calcd. on basis of original content of 1.7 acetate groups per glucose unit).

The above-described conditions were the mildest found that led to the complete removal of sulfur. Various other conditions, such as different times and temperatures of heating with acetonylacetone or heating at 80° with acetone, led to products containing none or varying amounts of sulfur (0 to 7%) but always nearly the same amount of iodine (0.3 to 0.4 atom of iodine per glucose unit, calcd. on basis of original content of 1.7 acetate groups per glucose unit).

Action of Aqueous Ammonia on Mesylated Cellulose and Mesyl Cellulose Acetate.—Mesylated cellulose and mesyl cellulose acetate were treated with aqueous ammonia under a variety of conditions but sulfur-free products were not obtained. Some typical experiments will be cited.

A low mesylated cellulose (5 g., 8.0% S) was suspended in 300 cc. of aqueous ammonia (28–29%) and heated on a steam-bath for twelve hours under reflux. The fibrous residue was removed by filtration and washed with hot water and acetone; yield 5 g.

Anal. S, 2.72; N (Dumas), 0.47.

Mesyl cellulose (1.0 g., 0.5 mesyl groups per glucose unit), regenerated from mesyl cellulose acetate by saponification according to the procedure of Malm and Clarke,[15] was treated for fifteen days at room temperature with 75 cc. of aqueous ammonia (28–29%). The filtered product was washed with water and absolute ethanol; yield 1 g. of a creamy-white, hygroscopic powder.

Anal. S, 6.50; N (Dumas), 1.29.

Mesyl cellulose acetate (5 g., 1.7 acetate and 1.0 mesyl groups per glucose unit) was suspended in 300 cc. of aqueous ammonia (28–29%) and heated on a steam-bath for six hours under reflux. The filtered material was washed with water and heated again with aqueous ammonia in the same manner. The filtered product was washed with hot water and dried at 50° under reduced pressure; yield 2.4 g. of a hygroscopic, light brown powder.

Anal. S, 5.0; N (Dumas), 3.67.

The assistance of Messrs. A. R. Hanze and E. J. Kohn in certain phases of this work is acknowledged.

Summary

1. Activated cellulose reacts with methanesulfonyl chloride in pyridine suspension to give a product approximating a dimethanesulfonate.

2. A study of the above reaction indicates no detectable point of initial primary alcohol esterification and it is shown that as the reaction proceeds the methanesulfonate groups are replaced by chlorine by reaction with the pyridine hydrochloride present. At room temperature and proper times, the chlorine replacement is negligible.

3. A modified pyridine-soluble cellulose acetate (1.7 acetyl groups per glucose unit) reacted readily with methanesulfonyl chloride in pyridine solution to produce a material containing one methanesulfonyl group per glucose unit.

4. The above mixed acetate, methanesulfonate of cellulose reacted with sodium iodide to form a product that was sulfur-free and contained 0.4 atom of iodine (18% iodine) per glucose unit.

5. The action of aqueous ammonia on cellulose methanesulfonate or on the above mixed acetate, methanesulfonate of cellulose, under various conditions, led to partial replacement of the methanesulfonate groups to yield products that contained appreciable amounts of sulfur (3 to 6%) and nitrogen (0.5 to 4%).

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