46. *The Reaction between Sodium Iodide and Toluenesulphonyl Derivatives of Glucofuranose.*

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Oldham and Rutherford (*J. Amer. Chem. Soc.*, 1932, **54**, 366) have shown that arylsulphonyl groups occupying position 6 in the glucopyranose chain are quantitatively replaced by iodine after two hours' heating at 100° with sodium iodide in acetone: under these conditions, groups in positions other than 6 are unaffected. As a means of identifying and eliminating 6-arylsulphonyl groups, this reaction has been employed by Oldham and Rutherford (*ibid.*, p. 1086), by Bell (J., 1934, 1177; 1936, 186), and, in a modified form, by Hess and Pfleger (*Annalen*, 1933, **507**, 48), Hess and Littman (*Ber.*, 1934, **67**, 465), and Hess and Eveking (*ibid.*, p. 1908).

Apart from reporting no reaction with 3-*p*-toluenesulphonyl diacetone glucose and with amorphous 5-*p*-toluenesulphonyl 2 : 3 : 6-trimethyl γ-methylglucoside, Oldham and Rutherford made no systematic examination in the furanose series. This we have now carried out, using crystalline glucofuranose derivatives, two of which are described for the first time. Treated according to Oldham and Rutherford, the following substances were recovered unchanged: 2-p-*toluenesulphonyl* 3 : 5 : 6-*tribenzoyl* β-*methylglucofuranoside*, 3-*p*-toluenesulphonyl diacetone glucose (Freudenberg and Ivers, *Ber.*, 1922, **55**, 929), and 5-*p*-toluenesulphonyl 6-acetyl monoacetone glucose (Ohle, Euler, and Lichtenstein, *Ber.*, 1929, **62**, 2885). Reaction ensued when the sulphonyl group occupied position 6, and, depending upon whether or not the adjacent 5-hydroxyl group was substituted, the products formed were of completely different type. 6-*p*-Toluenesulphonyl monoacetone glucose (Ohle and Dickhäuser, *Ber.*, 1928, **58**, 2593) yielded material free from iodine and sulphur, and with an unsaturated linkage. Further examination was not made, but it is suggested that the most probable product would be a derivative of 5 : 6-glucoseen. On the other hand, 6-p-*toluenesulphonyl* 3 : 5-*benzylidene monoacetone glucose* reacted smoothly to give the corresponding 6-*iodide* in good yield. The latter on heating in acetonitrile with silver *p*-toluenesulphonate re-formed the 6-*p*-toluenesulphonate.

Attempts to prepare, in the following manner, 5-toluenesulphonyl 3-methyl monoacetone glucose repeatedly ended in failure. 3-Methyl monoacetone glucose with *p*-toluenesulphonyl chloride in pyridine gave an amorphous product, which, with sodium iodide in acetone, gave largely sulphur-free derivatives together with a certain amount of a crystalline substance, tentatively described as 6-*chloro* 5-p-*toluenesulphonyl* 3-*methyl monoacetone glucose.* This substance was always formed when 3-methyl monoacetone glucose was toluenesulphonated, and could be isolated from the crude product without employing the sodium iodide reaction. It appears to be analogous to 6-chloro 2 : 3-di-*p*-toluenesulphonyl 4-acetyl α-methylglucoside (Littman and Hess, *Ber.*, 1934, **67**, 519) and resembles it in its stability. Neither the sulphonyl radicals nor the chlorine was affected by sodium iodide in acetone, nor was the chlorine replaced by toluenesulphonyl on boiling with the silver salt in acetonitrile.

Thus it appears that, in glucofuranose derivatives, as in the corresponding pyranose series, toluenesulphonyl groups occupying position 6 are alone reactive towards sodium iodide, with replacement by iodine, but only if the hydroxyl group of position 5 is adequately protected against the production of an unsaturated linkage.

EXPERIMENTAL.

Solvents were evaporated under reduced pressure, below 50°, polarimetric observations were made in chloroform solution in a 2 dm. tube, and substances were recrystallised to constant m. p. Heating with sodium iodide was carried out exactly as described by Oldham and Rutherford.

2-p-*Toluenesulphonyl* 3 : 5 : 6-*Tribenzoyl* β-*Methylglucofuranoside.*—3·9 G. of the crystalline 3 : 5 : 6-tribenzoyl glucofuranose–carbon tetrachloride addition compound of Fischer and Rund (*Ber.*, 1916, **49**, 88) were treated with 3 g. (3 mols.) of toluenesulphonyl chloride in pyridine for 24 hours. The crude tarry product was precipitated by the addition of water, well washed, dissolved in benzene and ether, and filtered through norit. The residue, after evaporation of the solvents, was dissolved in 25 ml. of acetic acid containing 50% of its weight of hydrobromic acid and kept for 6 hours. Benzene was added and the acetic and hydrobromic acids were washed out, first with water, and then with potassium bicarbonate solution. After dehydration over calcium chloride the benzene solution was concentrated to a thick syrup, which was mixed with methyl alcohol (10 vols.), shaken with silver carbonate for 2 hours, and kept over-night. Evaporation of the solvent yielded 1 g. of crystals. Recrystallised from ethyl alcohol, the *substance* formed fine needles, m. p. 125—127°, $[\alpha]_D^{20^\circ}$ − 61·9° (*c*, 4·5) (Found : S, 5·2; OMe, 4·5. $C_{35}H_{32}O_{11}S$ requires S, 4·8; OMe, 4·7%). The β-configuration is assigned on account of the method of synthesis and the strongly negative rotation.

6-p-*Toluenesulphonyl* 3 : 5-*Benzylidene Monoacetone Glucose.*—4 G. of 3 : 5-benzylidene monoacetone glucose (Brigl and Gruner, *Ber.*, 1932, **65**, 1428), dissolved in the minimum of pyridine, were treated with 1·5 mols. of finely powdered *p*-toluenesulphonyl chloride for 24 hours at room temperature. Water was then added and the crystals were separated, washed with water, and recrystallised from ethyl alcohol, forming needles (4 g.), m. p. 118°, $[\alpha]_D^{20^\circ}$ + 14·2° (*c*, 5) (Found : S, 6·9. $C_{23}H_{26}O_8S$ requires S, 6·9%).

6-*Iodo* 3 : 5-*Benzylidene Monoacetone Glucose.*—2 G. of the above toluenesulphonate were treated according to Oldham and Rutherford. The *product* (needles, 1·5 g.), recrystallised from ethyl alcohol, had m. p. 137°, $[\alpha]_D^{20^\circ}$ + 17·7° (*c*, 9·7) (Found : I, 12·9. $C_{16}H_{19}O_5I$ requires I, 30·3%). The iodo-compound, heated with silver toluenesulphonate in acetonitrile in a sealed tube at 100° for 12 hours, regenerated the toluenesulphonate, m. p. 118° alone or mixed with authentic material.

Chloro p-*Toluenesulphonyl* 3-*Methyl Monoacetone Glucose.*—20 G. of 3-methyl monoacetone glucose were treated with 82 g. of *p*-toluenesulphonyl chloride, dissolved in dry pyridine, for 5 days at 30°. After washing in benzene solution, the crude product was isolated as a dark-coloured glass which could not be crystallised. After extraction with much boiling ligroin, a dark residue remained undissolved. On allowing the ligroin to evaporate at room temperature, crystals were deposited : recrystallised from ethyl alcohol and acetone, 5 g. of needles were obtained, m. p. 143°, $[\alpha]_D^{15^\circ}$ − 46·6° (*c*, 7) (Found : OMe, 7·7; S, 7·5; Cl, 8·2. $C_{17}H_{23}O_7SCl$ requires OMe, 7·6; S, 7·8; Cl, 8·7%).

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