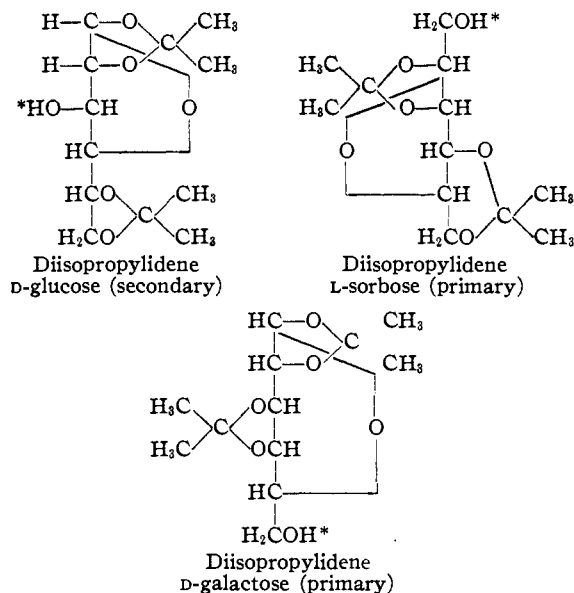


[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 271]

The Rates of Reaction of Diacetone Glucose, Diacetone Galactose and Diacetone Sorbose with *p*-Toluenesulfonyl Chloride in Pyridine Solution¹

BY ROBERT C. HOCKETT AND MASON L. DOWNING

In a previous publication² the "selective" action of triphenylchloromethane upon primary alcohols in pyridine solution as compared with the action of this chloride upon secondary alcohols, was interpreted as a difference in the rates of reaction of such alcohols under the conditions employed. This view was supported by direct rate measurements by polarimetric means upon the reactions between trityl chloride³ and the diisopropylidene derivatives of D-glucose, L-sorbose and D-galactose, respectively, in pyridine solution. All these compounds reacted when an eight to one molecular proportion of the chloride was used, the reactions were pseudounimolecular, and the times of half-change were in the ratio 226:6.6:1 in the order of their names.



On account of an apparent tendency among chemists to regard triphenylchloromethane as a quite peculiar or exceptional reagent, we thought it worth while to extend the study to an investigation of the rates of reaction of *p*-toluenesulfonyl chloride with the same sugar derivatives under the

same conditions.⁴ Such a study has yielded results which are compared with the previous ones below.

TABLE I

Substance	Rate constant (hours and dec. logs)		Times of half-change, hours	
	Trityl (21°)	Tosyl (23 ± 2°)	Trityl (21°)	Tosyl (23 ± 2°)
Diacetone glucose	0.00016	0.0149	1880.0	20.20
Diacetone sorbose	0.0055	0.5160	54.7	0.583
Diacetone galactose	0.036	1.038	8.3	0.272

1.00 g. substance in 50.0 pyridine solution 8:1 ratio of chloride;
2-dm. tube. $K = \frac{1}{t} \log_{10} \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$

The obvious conclusions are two: *p*-toluenesulfonyl chloride reacts faster with all the substances than does trityl chloride under the same conditions; the velocity ratios are of the same order of magnitude for the three substances in their reactions with either chloride. The rate ratio for the diacetone glucose and diacetone sorbose is 34.7/1 in the reaction with trityl chloride and 34.4/1 in the reaction with *p*-toluenesulfonyl chloride. Thus the latter appears to be equally "selective." More strictly speaking, the selectivity is a characteristic of the alcohols rather than of the halides.

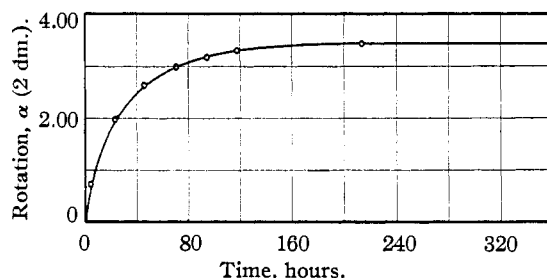


Fig. 1.—Diacetone-glucose and tosyl chloride at 23 ± 2°.

Much evidence is accumulating which tends to show that benzoyl chloride, acetic anhydride and other agents show much the same kind of selection.⁵

An extension of these measurements to other temperatures is in progress.

We express our indebtedness to Hoffmann-La Roche, Inc., of Nutley, N. J., for a quantity of diacetone-L-sorbose.

(1) This paper is taken from a thesis submitted by Mason L. Downing in partial fulfillment of the requirements for the Degree of Bachelor of Science in June, 1941.

(2) Hockett, Fletcher and Ames, *THIS JOURNAL*, **63**, 2516 (1941).

(3) "Trityl chloride" has become a widely accepted abbreviation for triphenylchloromethane.

(4) Cf. Compton, *THIS JOURNAL*, **60**, 395 (1938).

(5) Cramer, Hockett and Purves, *ibid.*, **61**, 3463 (1939); Brigl and Gruner, *Ber.*, **65**, 641 (1932).

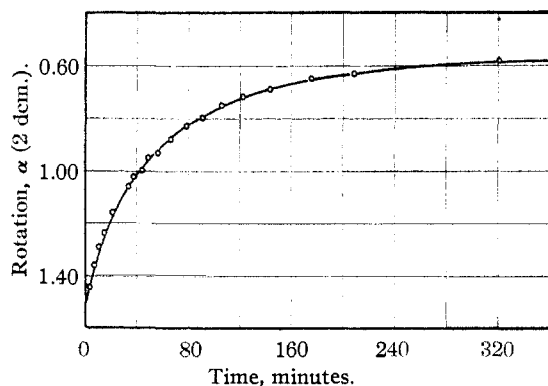


Fig. 2.—Diacetone-sorbose and tosyl chloride at $23 \pm 2^\circ$.

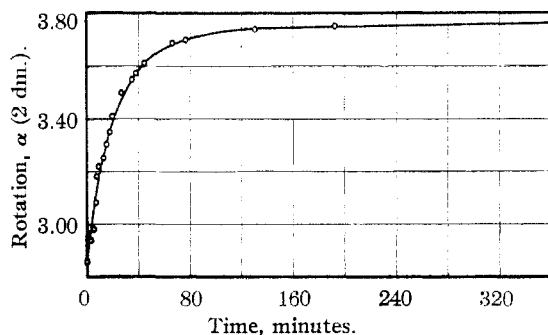


Fig. 3.—Diacetone-galactose and tosyl chloride at $23 \pm 2^\circ$.

Experimental

1,2;5,6-Diisopropylidene-D-glucofuranose.—A sample of this substance obtained from the Corn Products Refining Co., contained a considerable amount of monoacetone glucose. It was dissolved in water and extracted three times with very small portions of benzene to remove colored impurities. After a treatment with decolorizing carbon, the colorless aqueous solution was extracted five times with chloroform; the extract was dried with sodium

sulfate, filtered, and concentrated to crystallization. The product after a recrystallization from benzene and drying, melted from $109.5\text{--}110^\circ$ (cor.) and rotated⁶ -17.6° (c. 2.040; H_2O).

1,2;3,4-Diisopropylidene-D-galactopyranose.—This was prepared exactly as described previously.²

2,3;4,6-Diisopropylidene-L-sorbofuranose.—The dark-brown distillate supplied by Hoffmann-LaRoche was dissolved in ether and most of the coloring matter was removed by extractions with 20% KOH solution and then by carbon treatment. Almost colorless crystals were obtained when the dried ether extract was evaporated. A final recrystallization from petroleum ether (b. p. $30\text{--}60^\circ$) yielded white crystals melting from $77.5\text{--}78.5^\circ$.

Toluenesulfonyl Chloride.—Eastman Kodak Co. product melting $68.5\text{--}69.0^\circ$ (cor.) was employed.

Pyridine.—A colorless fraction dried over KOH and boiling at $115.3\text{--}115.5^\circ$ was used.

The Rate Measurements.—The method described for the case of triphenylchloromethane was duplicated.² The reactions took place in a constant-temperature room at $23 \pm 2^\circ$.

Summary

1. The rates of reaction of *p*-toluenesulfonyl chloride with diacetone glucose, diacetone sorbose and diacetone galactose at a molar ratio of 8 to 1 in pyridine solution, have been measured polarimetrically.

2. The reactions were pseudounimolecular and gave times of half-change in the ratio 74.2:2.1:1 in the order named.

3. The "selectivity" of *p*-toluenesulfonyl chloride toward primary hydroxyl groups as compared with secondary ones is of the same order as the "selectivity" of triphenylchloromethane.

(6) Specific rotation of the D line of sodium at 24° .

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Solubilities of Orthanilamide, Metanilamide and Sulfanilamide^{1a}

BY R. H. KIENLE AND J. M. SAYWARD^{1b}

In connection with a broad program of research on chemotherapeutic agents of the sulfanilamide type, a study of certain physical chemical properties of sulfanilamide and its therapeutically inactive isomers was undertaken. Any distinction found between the active para compound and the inactive ortho and meta isomers might contribute to the explanation of the therapeutic activity of sulfanilamide.

(1a) Presented at the 103rd meeting of the American Chemical Society, Memphis, Tenn., April, 1942.

(1b) Present address: Stamford Research Laboratories, American Cyanamid Company, Stamford, Connecticut.

The present paper reports on the water-solubilities of the three sulfanilamide isomers. The results led to dilatometry and manometric drying of the solid phase of sulfanilamide. Microscopical and X-ray investigation of the three isomers is expected to be published at a later date by our Laboratories. Solubilities were also determined at 37° in buffered solutions.

Experimental

Materials.—Sulfanilamide (U. S. P.) from plant production was recrystallized from alcohol and from hot water.

Orthanilamide was synthesized by standard methods