tallized. The results of those determinations are recorded in Table I.

2,15-Diphenyl-1,3,14,16-tetrathiacyclohexacosane Tetrasulfone.—The cyclic dimercaptal was oxidized to the corresponding tetrasulfone by the method of Drew.[9] A mixture of 2.90 g. (0.0049 mole) of the cyclic mercaptal and 350 ml. of a 0.14 *M* solution (0.049 mole) of monoperphthalic acid[9,10] in dry ethyl ether was placed in an erlenmeyer flask fitted with a magnetic stirrer and a soda-lime tube, and stirred for 24 hours at room temperature. Additional dry ether (200 ml.) and 100 ml. of the monoperphthalic acid solution were added and the mixture was stirred for 24 hours. A final 250-ml. portion of the monoperphthalic acid solution was added and the mixture was stirred for still another 48 hours.

The product was collected on a filter, affording 3.36 g. (95%) of white solid, m.p. 189–191°. After several recrystallizations from chloroform, the analytical sample had m.p. 195–196°.

Anal. Calcd. for $C_{34}H_{52}S_4O_8$: C, 56.95; H, 7.31; S, 17.89. Found: C, 57.46; H, 7.39; S, 18.32.

The same tetrasulfone was obtained in lower yield by an acid permanganate oxidation of the cyclic mercaptal.

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[9] H. F. Drew, Ph.D. Thesis, University of Minnesota, Minneapolis, Minn., November, 1951, p. 52.

[10] H. Böhme, *Org. Syntheses*, **20**, 70 (1940).

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2,5-Dimethyl-D-glucofuranose and Two New Crystalline Derivatives

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In connection with studies on the flameproofing of cotton fiber by reaction with titanium compounds it was desired to investigate, separately, the reactivity of the various glucoside hydroxyl pairs with titanium. This was accomplished by the use of model glucosides having all but two positions blocked by substituent groups. One of the model glucosides employed for this purpose was methyl 2,5-dimethyl-α-D-glucofuranoside, which has not previously been described in the literature. Its preparation and properties are described in this note. Its reactivity with organic titanates will be considered in a separate communication together with the reactivity of cellulose and several other model glucosides.

In a review article published in 1950, Bourne and Peat[1] were able to list all but three of the twenty-three possible methyl ethers of D-glucofuranose and D-glucopyranose as having been prepared in pure form or in the form of a closely related derivative. One of the three glucose ethers which had not been reported at that time was 2,5-dimethyl-D-glucofuranose, whose only known derivatives were in the distantly related glucuronic acid and 3,6-anhydroglucose series. This report records the preparation of two crystalline derivatives of 2,5-dimethyl-D-glucofuranose: namely, methyl 2,5-dimethyl-α-D-glucofuranoside and its 3,6-diacetate. From either of these derivatives the parent dimethyl glucose ether may be obtained in solution upon hydrolysis. Attempts to isolate the reducing sugar in crystalline condition have so far been unsuccessful, apparently because it undergoes self-condensation when water is evaporated from its aqueous solutions.

The structures of the new derivatives are established only by their method of synthesis, the reduction of methyl 2,5-dimethyl-α-D-glucurone with lithium aluminum hydride. They have not been directly related with any other known glucose derivatives. However, since the reduction would not be expected to alter the configuration at any of the asymmetric centers, assignment to the glucose series can be made with considerable assurance.

Experimental

Methyl 2,5-Dimethyl-α-D-glucofuranoside.—Three grams of lithium aluminum hydride was suspended in 100 ml. of dry ether in a flask attached to an extraction apparatus. A quantity of 2.13 g. of methyl 2,5-dimethyl-α-D-glucurone[2,3] was placed in a sintered glass thimble which was located in the extraction apparatus so that the ether upon refluxing slowly transferred the glucurone to the slurry of reducing agent. After refluxing for six hours and standing at room temperature overnight the excess lithium aluminum hydride was destroyed with 300 ml. of moist ether. Filtration and extraction of the precipitated hydroxides yielded an ether solution of the product which upon concentration deposited 1.44 g. of crystals. Recrystallization from ether gave a product melting between 55° and 72°. At 0.001 mm. it distilled at about 70° (bath) and the distillate crystallized readily on the condenser. In most cases the distillate melted sharply at 55–57°, but in some experiments a higher melting form, m.p. 70–72°, was encountered. The higher melting form could also be obtained by recrystallization from ether, but it gradually changed to the lower melting form on standing. Both forms displayed the same specific rotations (sodium D line, 25°) which were as follows: in methanol, +140° (*c* 1.0); in ether, +157° (*c* 1.0); in water, +124° (*c* 0.87).

Anal. Calcd. for $C_9H_{18}O_6$ (222.23): C, 48.64; H, 8.16; OCH_3, 41.89. Found: C, 48.59, 48.30; H, 8.27, 8.14; OCH_3, 41.35, 41.39.

The glucoside did not contain any saponifiable ester or lactone.

Methyl 2,5-Dimethyl-3,6-diacetyl-α-D-glucofuranoside.—A quantity of the above methyl glucoside weighing 1.19 g. was dissolved in 4 ml. of pyridine and treated with 2 ml. of acetic anhydride. The solution was warmed to 80° for two hours, then evaporated to dryness in vacuum. The sirupy residue crystallized from a mixture of ether and petroleum pentane; yield 0.64 g. After recrystallization from the same solvent this material had a very sharp melting point of 46–47°. Its specific rotation in chloroform was +95° (*c* 2.6), and in ether, +133° (*c* 3.6).

Anal. Calcd. for $C_{13}H_{22}O_8$ (306.31): C, 50.97; H, 7.24; CH_3CO, 28.1. Found: C, 50.91, 51.05; H, 7.24, 7.23; CH_3CO (by saponification and back titration), 28.5, 28.4.

Deacetylation of this substance with a trace of sodium methoxide in methanol yielded the original glucoside, m.p. 55–56°; sp. rot. in ether, +158°.

2,5-Dimethyl-D-glucofuranose by Hydrolysis of Its Glucoside. (a) With Hydrochloric Acid.—Twenty-six mg. of the glucoside, dissolved in 2.4 *N* hydrochloric acid, changed in 90 minutes at room temperature from strongly dextrorotatory to zero rotation. In another experiment 300 mg. of the glucoside in *N* hydrochloric acid reached a constant zero rotation on standing overnight at room temperature. The chloride ion was removed on a small column of Amberlite 400[4] resin and the solution evaporated to dryness. The residue of 163 mg. of a colorless sirup failed to crystallize on standing.

(b) **With Amberlite 120H.**[4]—In this experiment 628 mg. of the crystalline glucoside was dissolved in 25 ml. of water and treated with 1 g. of moist Amberlite 120H resin which previously had been boiled with several changes of distilled water. Upon refluxing, the rotation of the solution changed

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[1] E. J. Bourne and S. Peat, *Advances in Carbohydrate Chemistry*, **5**, 145 (1950).

[2] J. Pryde and R. T. Williams, *Biochem. J.*, **27**, 1205 (1933).

[3] R. E. Reeves, THIS JOURNAL, **62**, 1616 (1940).

[4] The mention of a trade product does not imply its endorsement by the Department of Agriculture over similar products not named.

during one hour from +2.40° to +0.06° and remained unchanged upon further boiling. This corresponds to a specific rotation of +3° for the dimethylglucose in water (*c* 2). The resin was removed by filtration and the water evaporated in vacuum. It was dried over P_2O_5, leaving 490 mg. of colorless sirup which failed to crystallize.

The freshly hydrolyzed solutions were strongly reducing toward alkaline hypoiodite, Hagedorn–Jensen[5] solution and hot Fehling solution. They would not, however, reduce Fehling solution in the cold, nor restore color to a decolorized fuchsin–sulfurous acid solution. The sirups obtained after evaporation of the water showed greatly decreased reducing activity, but the reduction was restored upon boiling the sirups in dilute acid solution.

A drop of the freshly hydrolyzed 2,5-dimethylglucofuranose solution was placed on a strip of filter paper which was then developed as a descending chromatogram with the butanol–formic acid and water reagent of Wiggins and Williams.[6] The substance, moving as a single spot, travelled 5 or 6 times as far as glucose under comparable conditions. The color of the spot was developed with aniline hydrogen phthalate. Both the unhydrolyzed glucoside and the sirup obtained after hydrolyzing and drying failed to give a color with the aniline hydrogen phthalate reagent, but after hydrolysis with dilute acid both gave the same fast-moving dimethylglucose.

Acknowledgment.—The micro carbon and hydrogen analyses were performed by Lawrence E. Brown, and the methoxyl analyses by J. W. Weaver. Laurence W. Mazzeno, Jr., assisted with the reducing sugar determinations and E. A. Schoenhardt, Jr., with the paper chromatography.

[5] C. S. Hanes, *Biochem. J.*, **23**, 99 (1929).

[6] L. F. Wiggins and J. H. Williams, *Nature*, **170**, 279 (1952).

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Reactions of Diazo Compounds with Nitroölefins. IV. The Decomposition of Diphenyldiazomethane

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The reaction of diphenyldiazomethane with nitroölefins to give nitropyrazolines[2] is complicated, in certain cases, by decomposition of the diazocompound. For example, it was found that diphenyldiazomethane does not react with 1-phenyl-2-nitropropene-1 to give the expected pyrazoline. When the reaction was carried out in benzene, only benzophenone azine, a known decomposition product of diphenyldiazomethane,[3] and unreacted nitroölefin were obtained. When hot petroleum ether was employed as solvent, *sym*-tetraphenylethane and a molecular complex of this substance and benzophenone azine were obtained in addition to benzophenone azine and starting material. Neither *sym*-tetraphenylethane nor the molecular complex described had previously been reported as decomposition products of diphenyldiazomethane. That they were not derived from the nitroölefin was shown by the isolation of the same products from similar reactions conducted in the absence of the olefin.

Isolation of *sym*-tetraphenylethane from reactions employing hot petroleum ether as solvent, and failure to obtain this product from reactions employing benzene as solvent or reactions effected without solvent, suggested the following course for the decomposition of the diazo compound.

$$(C_6H_5)_2CH_2N_2 + \underset{\text{I}}{(C_6H_5)_2C:}$$

$$\text{I} \xrightarrow{\text{solvent}} (C_6H_5)_2CH\cdot \longrightarrow \underset{\text{II}}{(C_6H_5)_2CHCH(C_6H_5)_2}$$

There was no evidence for the formation of tetraphenylethylene[4] which might be expected to result directly from I.

Evidence which constitutes proof of structure of the molecular complex of *sym*-tetraphenylethane and benzophenone azine is described in the Experimental section. Examination of the ultraviolet spectra of the molecular complex indicated that there was no interaction between the two components in dilute solution in ethanol. At each wave length the extinction coefficient was the sum of those of its components. Jones and Neuworth[5] reported a similar behavior for the 1,3,5-trinitrobenzene derivatives of naphthalene, anthracene, etc.

Experimental

Attempts to Add Diphenyldiazomethane to 1-Phenyl-2-nitropropene-1.—The results are summarized in Table I. In each case 1.60 g. (0.0098 mole) of olefin was treated with 2.20 g. (0.0113 mole) of diphenyldiazomethane. The reactions were allowed to proceed until the red color of the diazo compound disappeared. The products were separated by crystallization from petroleum ether, and further purified by recrystallization from petroleum ether, benzene or ethanol.

Table I

Run	Solvent	Temp., °C.	Time of reacn.	Benzophenone azine, m.p. 162–164°, g.	*sym*-Tetraphenylethane, m.p. 211–212°, g.	Molecular complex, m.p. 177–177.5°, g.	Unchanged olefin, g.
1	Pet. ether	120	30 min.	0.50	0.15	0.05	..
2	Pet. ether	55	9.5 days	.38	.05	.32	..
3	Pet. ether	22	6 mo.	.90	..	..	0.10
4	None	22	1 mo.	.95	..	..	1.33

Decomposition of Diphenyldiazomethane in Benzene.—A solution of diphenyldiazomethane (2.7 g., 0.014 mole) in benzene (50 ml.) was heated at the reflux temperature until the red color of the diazo compound had disappeared (five days). The benzene was removed by distillation and the residual solid was recrystallized from ethanol. There was obtained 2.0 g. (74% yield) of benzophenone azine, m.p. 163–163.5°. Neither *sym*-tetraphenylethane or the complex of azine and hydrocarbon could be detected in the reaction product.

Decomposition of Diphenyldiazomethane in Petroleum Ether.—A solution of diphenyldiazomethane (4.7 g., 0.024 mole) in petroleum ether was heated at 120° (reflux) for 2.5 hours (the red color disappeared after 90 minutes). The mixture was cooled and 1.9 g. (45% yield) of yellow crystals, m.p. 157–173°, was removed by filtration. The solid melted at 177–177.5° after recrystallization from ethanol and did not depress the melting point when admixed with the 1:1 molar complex of benzophenone azine and *sym*-tetraphenylethane.

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[1] From the Ph.D. Thesis of William R. Hasek, University of Minnesota, 1953.

[2] W. E. Parham and W. R. Hasek, This Journal, **76**, 799 (1954).

[3] T. Curtius and F. Rauterberg, *J. prakt. Chem.*, [2] **44**, 192 (1891).

[4] Benzophenone azine has been previously reported as the only product resulting from the decomposition of diphenyldiazomethane. However, di-(*p*-methoxyphenyl)-diazomethane and 9-diazofluorene give tetra-(*p*-methoxyphenyl)-ethylene and difluorenylidene, respectively. *Cf.* H. Staudinger and O. Kupfer, *Ber.*, **44**, 2197 (1911).

[5] R. C. Jones and M. B. Neuworth, This Journal, **66**, 1497 (1944).