Aryl Carbamate Derivatives of D-Glucosan $<1,5>\beta<1,6>$ and of 1,2-Isopropylidene-D-glucose

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In connection with other studies on the reactions of carbohydrates with aromatic isocyanates, levoglucosan tricarbanilate and tri-N-α-naphthylcarbamate, and 1,2-isopropylidene-D-glucose tricarbanilate and tri-N-α-naphthylcarbamate have been prepared.

The completely substituted derivatives were easy to prepare in good yield and were quite insoluble in water. They were best purified either by precipitation with water from their acetone or dioxane solutions or by digestion with organic solvents in which they were insoluble. All these derivatives could be crystallized from either glacial acetic or propionic acid solutions. However, the materials crystallized slowly, and the products, although analytically pure, had lower and less sharp melting points than those purified as described. Data on the products are collected in Table I.

TABLE I

Compound ⟶			Levoglucosan tricarbanilate	1,2-Isopropylidene-D-glucose tricarbanilate	Levoglucosan tri-N-α-naphthylcarbamate	1,2-Isopropylidene-D-glucose tri-N-α-naphthylcarbamate
M. p., °C.			234–235	258–259	270–271.5	238.5–240
$[\alpha]^{25}$D in pyridine		Deg.	−44.9	−6.1	−25.3	−77.7
		c =	1.791	0.961	1.060	0.762
Formula			$C_{27}H_{25}O_8N_3$	$C_{30}H_{31}O_9N_3$	$C_{39}H_{31}O_8N_3$	$C_{42}H_{37}O_9N_3$
Analyses, %	Carbon	Calcd.	62.4	62.4	70.0	69.3
		Found	62.3	62.5	69.9	69.1
	Hydrogen	Calcd.	4.8	5.4	4.6	5.1
		Found	4.8	5.4	4.9	5.0
	Nitrogen	Calcd.	8.1	7.3	6.3	5.8
		Found	8.0	7.2	6.4	5.6

The stability of the aryl carbamate grouping toward mild acid and alkaline reagents[1] suggests the possible use of the esters here reported in the preparation of selectively substituted glucose derivatives of known structure.

Experimental

Levoglucosan Tricarbanilate.—A mixture of levoglucosan (1.62 g., 10 millimoles) and dry pyridine (15 ml.) was treated with phenyl isocyanate (4 g., 33.6 millimoles) and allowed to stand at room temperature for three days. Ten ml. of methanol was added, the mixture was warmed for ten minutes on a steam-bath, and then poured into approximately 150 ml. of water. The resulting white precipitate was dissolved in hot acetone. On cooling, 1.8 g. of amorphous solid separated. One further precipitation of this material from acetone gave an analytically pure product. Evaporation of the first mother liquors gave two additional crops, weighing 2.9 g., or a total of 90% of the theoretical amount.

1,2-Isopropylidene-D-glucose-tricarbanilate.—A mixture of 1,2-isopropylidene-D-glucose (2.20 g., 10 millimoles), dry pyridine (25 ml.) and phenyl isocyanate (5.4 g., 45.3 millimoles) was allowed to stand overnight. Ten ml. of methanol was added. After the mixture had stood for several hours a voluminous precipitate formed. The mixture was poured into approximately 150 ml. of methanol and filtered, giving 5.05 g. (87.5% of theory) of product which melted sharply at 258–259°. Solution in dioxane and reprecipitation with water gave a product of unchanged melting point, which was analytically pure.

Levoglucosan Tri-N-α-naphthylcarbamate.—Traces of water were removed from 3.24 g. (20 millimoles) of levoglucosan by azeotropic distillation, using pyridine. The mixture (containing 100 ml. of pyridine at this point) was cooled to 100°, and 15 g. (88.8 millimoles) of α-naphthyl isocyanate was added. Reaction was carried out at 100° with stirring for three and one-half hours, after which the oil-bath was removed and 10 ml. of methanol was added to the hot mixture. After standing overnight the mixture was filtered, the filtrate was evaporated to dryness *in vacuo*, and this solid was then digested with 200 ml. of boiling acetone and filtered. The residue weighed 12.1 g., representing a 90% yield of crude levoglucosan tri-N-α-naphthylcarbamate. An analytically pure sample was prepared by solution of the crude material in dioxane, reprecipitation with water, and extraction of the reprecipitated material with hot acetone.

1,2-Isopropylidene-D-glucose Tri-N-α-naphthylcarbamate.—Reaction was carried out as above, using 4.4 g. (20 millimoles) of 1,2-isopropylidene-D-glucose, 100 ml. of pyridine, and 15 g. (88.8 millimoles) of α-naphthyl isocyanate. The cooled reaction mixture was poured into 500 ml. of absolute ethanol and the clear solution was then added to 1 liter of water. The crude product which precipitated weighed 14.9 g. This material was dissolved in boiling acetone (700 ml.) and reprecipitated with 2 volumes of water, giving 13.4 g. of 1,2-isopropylidene-D-glucose tri-N-α-naphthylcarbamate, melting at 226–233°. An analytically pure sample was obtained by twice redissolving the crude product in dioxane and reprecipitating with water, followed by extraction of the reprecipitated material with boiling ethanol.

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[1] Hearon, Hiatt and Fordyce, THIS JOURNAL, 66, 995 (1944).

Willgerodt–Kindler Reaction with a Pyrrole

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The preparation of pyrroles containing acetic acid substituents is of interest because of the struc-