

comp. 169 to 173 °C, (recrystallized from a little glacial acetic acid) explodes extremely violently on rapid heating.

Received, April 8th, 1963 [Z 490/316 IE]

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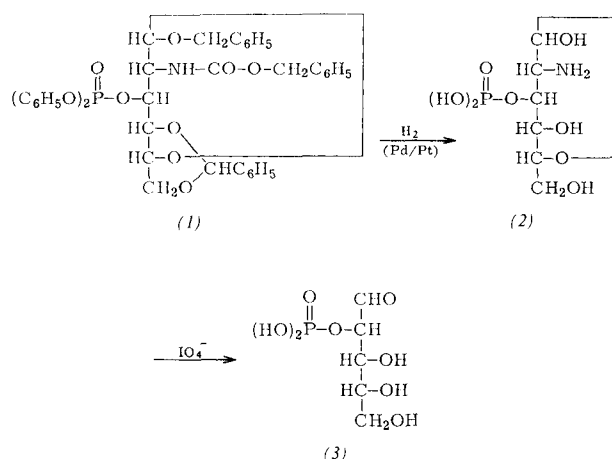
Synthesis of D-Glucosamine-3-phosphate

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D-Glucosamine-4-phosphate has been identified as a unit in the lipid component (lipid A) [2] of lipopolysaccharides from Gram-negative bacteria (endotoxin complexes) [3]. Of all the glucosamine phosphates, only the 6-phosphate had previously been identified and synthesized [4], hence we started work upon the synthesis of further glucosamine phosphates and have first prepared the 3-phosphate (2). Benzyl *N*-carbobenzoxyglucosaminide [5] was converted with benzaldehyde/ZnCl₂ into benzyl *N*-carbobenzoxy-4,6-*O*-benzylidene-glucosaminide, and treatment of this with diphenylphosphonyl chloride in pyridine gave rise to benzyl *N*-carbobenzoxy-3-diphenylphosphoryl-4,6-*O*-benzylidene-glucosaminide (1) in about 80% yield. Chromatography on silica gel with 2% methanol in benzene gave two crystalline fractions, one with $[\alpha]_D^{20} = +37.5^\circ$ and m.p. 98 °C and the other with $[\alpha]_D^{20} = -39.0^\circ$ and m.p. 125 °C (chiefly α - and β -forms).

Without using strong acids, which displace the phosphoric ester group from C-3 to C-6, it was possible to convert (1) into (2) by hydrogenolysis. Compound (1) was first hydrogenated in ethanol at room temperature with Pd-black. Water was then added up to 33% (vol.) and hydrogenation continued at 50 °C and finally for 0.5 hour at 60 °C after addition of acetic acid to a concentration of 40%. The resulting crude glucosamine-3-diphenylphosphate was hydrogenated in absolute alcohol with Pt-black at room temperature. Glucosamine-3-phosphate (2) was purified by chromatography on cellulose powder with ethanol/water (1:1). We obtained (2) in 25–30% yield, calc. from (1). It was taken up in a very small amount of water, and the solution treated with acetone. Needles of (2) crystallized out in the cold, m.p. about 180 °C (decomp.); $[\alpha]_D^{20} = +70 \pm 5^\circ$ ($c = 0.03$ in water), no mutarotation.



Acetylation in pyridine/acetic anhydride produced a good yield of crystalline tetraacetate, m.p. 148–150 °C (from ethanol/ether).

High-voltage electrophoresis of (2) on paper between pH 3 and 8 showed it to be homogeneous and different from glucosamine-6-phosphate. Degradation of (2) with periodate [6] yielded D-arabinose-2-phosphate (3), which behaved on paper chromatography (ethanol/water/acetic acid, 80:15:5) and in high voltage electrophoresis like the degradation product of D-glucose-3-phosphate [7] and which was different from D-arabinose-3-phosphate (obtained by degradation of D-glucose-4-phosphate with periodate [7]) and from arabinose 5-phosphate [3]. In the Elson-Morgan test, (2) gives a significantly weaker color reaction as compared to free glucosamine (only about 30%; the intensity increases on further hydrolysis).

Lambert and Zilliken [8] have also synthesized (2) independently by a similar route.

Received, April 24th, 1963 [Z 488/315IE]

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O-Alkylnitrosoimmonium Salts, a New Class of Compounds

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By analogy to the smooth *O*-alkylation of *N,N*-dialkylcarboxamides [2], *N,N*-dialkyl-*N*-nitrosamines react with triethylxonium fluoroborate [3] in ethylene chloride, or with methyl or ethyl iodide and silver perchlorate in nitromethane to give the immonium salt (1) by *O*-alkylation. The salts (3)–(8) exhibit a characteristic band at 1540–1575 cm⁻¹ which can be attributed to the mesomeric system in (1). The tautomeric form (2) is absent because there is no band between 1600 and 1700 cm⁻¹ ($>C=N^{\oplus}<$ [4]) nor between 3050 and 3500 cm⁻¹ ($>N-H$). Moreover, proton resonance spectra show that (4), (5), and (7) have two equal methylene groups adjacent to the hetero nitrogen atom. The salts dissolve without decomposition even in hydroxylic solvents but evolve nitrogen in strong bases. Salt (4) consumes two

Table 1. *O*-Alkylnitrosoimmonium salts

		M. p. [°C]	Infrared absorption [cm ⁻¹]	Yield [%]	
(3)	$(\text{CH}_3)_2\text{N}::\overset{\oplus}{\text{N}}\cdots\text{O}-\text{C}_2\text{H}_5$	BF_4^{\ominus}	36–39	1575	93
(4)	$(\text{CH}_2)_4\text{N}::\overset{\oplus}{\text{N}}\cdots\text{O}-\text{C}_2\text{H}_5$	BF_4^{\ominus}	66–67	1570	97
(5)	$(\text{CH}_2)_5\text{N}::\overset{\oplus}{\text{N}}\cdots\text{O}-\text{C}_2\text{H}_5$	BF_4^{\ominus}	50.5–51	1562	91
(6)	$(\text{CH}_2)_5\text{N}::\overset{\oplus}{\text{N}}\cdots\text{O}-\text{CH}_3$	ClO_4^{\ominus}	59–61	1560	92
(7)	$(\text{C}_6\text{H}_5-\text{CH}_2)_2\text{N}::\overset{\oplus}{\text{N}}\cdots\text{O}-\text{C}_2\text{H}_5$	BF_4^{\ominus}	oil	1540 [a]	98
(8)	$(\text{C}_6\text{H}_5-\text{CH}_2)_2\text{N}::\overset{\oplus}{\text{N}}\cdots\text{O}-\text{CH}_3$	ClO_4^{\ominus}	101–102	1540	96

[a] Film, others in Nujol.