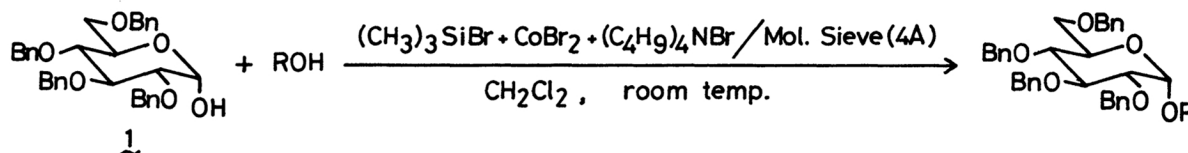


ONE-STAGE α -GLUCOSYLATION USING TETRA-O-BENZYL- α -D-GLUCOSE
AND MIXTURE OF TRIMETHYLSILYL BROMIDE, COBALT(II) BROMIDE,
TETRABUTYLAMMONIUM BROMIDE, AND MOLECULAR SIEVE

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The one-stage α -glucosylation using 2,3,4,6-tetra-O-benzyl- α -D-glucopyranose and a mixture of trimethylsilyl bromide, cobalt(II) bromide, and tetrabutylammonium bromide in the presence of molecular sieve is presented.

A variety of α -glucosylation reactions starting from 2,3,4,6-tetra-O-benzyl- α -D-glucopyranose (1) have been reported.¹⁾ However, none of them can be performed in one-stage fashion; they always require the activation stage^{1a)} or the preparation of an intermediate.^{1b,c)} We now wish to communicate the one-stage²⁾ α -glucosylation procedure using 1 and a composed reagent system of trimethylsilyl bromide, cobalt(II) bromide, and tetrabutylammonium bromide in dichloromethane containing molecular sieve (4A)

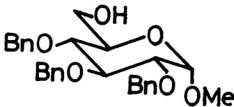
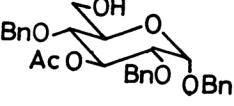
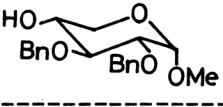


A typical procedure is as follows: To a mixture of 1 (90 mg, 0.17 mmol), cyclohexylmethanol (16 μ l, 0.13 mmol), cobalt(II) bromide (37 mg, 0.17 mmol), tetrabutylammonium bromide (54 mg, 0.17 mmol), and molecular sieve (4A, 135 mg) in dichloromethane (0.45 ml), trimethylsilyl bromide (18 μ l, 0.17 mmol) was added and the resulting mixture was stirred overnight at room temperature in the dark. After filtration, the reaction mixture was concentrated and chromatographed on silica gel as usual.

Table 1 shows the results of α -glucosylation of some alcohols including monosaccharide derivatives using this handy procedure.

The equimolar mixture of trimethylsilyl bromide and cobalt(II) bromide converted 1 rapidly into 2,3,4,6-tetra-O-benzyl- α -D-glucopyranosyl bromide (2). The ternary reagent system apparently brominates 1, in the presence of alcohol, into 2 which undergoes the halide-catalyzed α -glucosylation.³⁾

Table 1 Results of Glucosylation¹

Alcohol (ROH)	Reaction Time h	Yield of glucosides ² %
Cyclohexylmethanol	16	100 (76) ³
Cyclohexanol	16	90 (80) ³
5 α -Cholestan-3 β -ol	16	87 (72) ⁴
6-(2,4-Dinitroanilino)hexanol	16	94 (73) ⁴
	16	69 (85) ⁵
	42	73 (86) ^{6,7}
	42	36 (82) ^{7,8}

¹ Mol ratio of 1, CoBr₂, (CH₃)₃SiBr, and (C₄H₉)₄NBr to alcohol (ROH) was 1.3 and weight ratio of the molecular sieve to 1 was 1.5. ² The value in parenthesis is the weight % of the α -anomer. ³ Glucosides were identified with those reported in ref. 2c. ⁴ Glucosides were identified with those reported in ref. 2d.

⁵ Glucosides were identified with those reported in rer. 2a. The α -anomer, mp 105-106 °C, [α]_D²⁰+59 °(c 1.0, CHCl₃) [lit.^{1b}) mp 101.5 °C, [α]_D²⁰+59.3 °(c 1.78, CHCl₃)].

⁶ The α -anomer, mp 119-121 °C, [α]_D²⁰+88 °(c 1.0, CHCl₃), the β -anomer mp 99-101 °C, [α]_D²⁰+22 °(c 0.6, CHCl₃). ⁷ Glucosides gave correct analysis. ⁸ The α -anomer, [α]_D²⁰+58 °(c 1.0, CHCl₃), the β -anomer, [α]_D²⁰+38 °(c 1.5, CHCl₃).

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