

381. *N*-Substituted Glycosylamines. Part III.* Acetates, Benzoates, and Methyl Ethers.

By G. P. ELLIS and JOHN HONEYMAN.

Acetylation of *N*-*p*-tolylglucosylamine, followed by hydrolysis, leads to glucose 2 : 3 : 4 : 6-tetra-acetate.

Methods for the preparation of crystalline benzoates of *N*-arylglucosylamines are described for the first time, together with their conversion into the corresponding aldose benzoate. In this way *N*-*p*-tolylglucosylamine has been converted into glucose 2 : 3 : 4 : 6-tetra-benzoate, *N*-*p*-tolylmannosylamine into mannose 2 : 3 : 4 : 6-tetra-benzoate, and *N*-*p*-tolylxylosylamine into xylose 2 : 3 : 4-tribenzoate.

Several different ways, including direct methylation, have been used to prepare tetramethyl ethers of *N*-phenyl- and *N*-*p*-tolyl-glucosylamines and in all cases the crystalline products have been pyranose compounds with high positive specific rotations.

In all the reactions investigated, the *N*-arylglucosylamines react as pyranose compounds.

THE acetates of *N*-arylglucosylamines have been prepared in several ways and since, in contrast to the parent compounds, they are stable, crystalline, and sharp-melting, they have been used in some cases as derivatives for characterization (Frèrejacque, *Compt. rend.*, 1938, **206**, 111). Those reported are pyranoses since they can also be prepared from aldopyranose acetates and from acetobromoaldopyranoses. The acetates obtained by acetylation of the *N*-arylglucosylamines may be the α - or the β -anomer or a mixture of both. In syntheses using the acetobromo-sugar, the β -anomer is invariably produced (Kuhn and Dansi, *Ber.*, 1936, **69**, 1745; Butler, Smith, and Stacey, *J.*, 1949, 3371; Honeyman and Tatchell, *J.*, 1950, 967), whereas Butler *et al.* obtained the α -anomer by the interaction of tetra-acetyl D-galactose with the amine. In the present work it has been found that 2 : 3 : 4 : 6-tetra-acetyl D-glucose reacts with aniline to give *N*-phenyl- α -D-glucopyranosylamine tetra-acetate and with *p*-toluidine to give *N*-*p*-tolyl- β -D-glucopyranosylamine tetra-acetate, each in good yield. Acetylation of *N*-*p*-tolyl-D-glucosylamine with excess of acetic anhydride gives *N*-*p*-tolyl- β -D-glucosylamine tetra-acetate (Honeyman and Tatchell, *loc. cit.*). An attempt to extend the method of Butler *et al.* (*loc. cit.*), by which they obtained a mixture of α - and β -anomers of *N*-phenylgalactosylamine tetra-acetate, gave the β -anomer only.

Zemplén and Gerecs (*Ber.*, 1930, **63**, 2720) obtained a high proportion of α -anomer from the interaction of hepta-acetyl cellobiosyl bromide with alcohols in the presence of mercuric acetate. An attempt was made in the present work to adapt this reaction to the case of acetobromoglucose and *p*-toluidine but in all cases except one the β -isomer, $[\alpha]_D -33^\circ$ in chloroform, was isolated. In one experiment, a very small amount of an unidentified dextrorotatory product, $[\alpha]_D +70.6^\circ$ in chloroform, was obtained but the yield made the method impracticable.

Crystalline benzoates of *N*-substituted glycosylamines have not been reported. The method used here consists of treating a pyridine solution of the compound with a small excess of benzoyl chloride at 0° for from 15 minutes to 3 hours. In this way, crystalline benzoates of *N*-*p*-tolyl-D-xylosylamine, -glucosylamine, and -mannosylamine have been obtained, but benzylation of *N*-phenyl-D-glycosylamine and -ribosylamine gave benzanilide as the sole product isolated. *N*-*p*-Tolylglucosylamines give crystalline benzoates more readily than do the *N*-phenyl derivatives which are, apparently, hydrolysed. The crystalline benzoates described are stable, well-defined, high-melting solids, and as they are obtained in good yield are suitable for characterization of *N*-arylglucosylamines.

Removal of the amine group from the esters is a useful method for locating the position of the ring. In the present work, the hydrolysis of *N*-*p*-tolyl-D-glucosylamine tetra-acetate to crystalline 2 : 3 : 4 : 6-tetra-acetyl D-glucose, m. p. 124—126°, in good yield is reported. Variations in the melting point of this compound have been recorded: thus

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Hendricks, Wulf, and Liddell (*J. Amer. Chem. Soc.*, 1936, **58**, 1997) give values ranging from 114—117° to 138—140°. This route to 2 : 3 : 4 : 6-tetra-acetyl D-glucose is an attractive alternative to the standard method through acetobromoglucose (*Org. Synth.*, 1945, **25**, 53). Similarly, *N-p*-tolyl-D-glucosylamine tetrabenzoate has been converted into 2 : 3 : 4 : 6-tetrabenzoyl D-glucose, identical with that prepared from 2 : 3 : 4 : 6-tetrabenzoyl glucosyl bromide by Fischer and Noth (*Ber.*, 1918, **51**, 332). Hydrolysis of *N-p*-tolyl-D-mannosylamine tetrabenzoate in the same way gave 2 : 3 : 4 : 6-tetrabenzoyl D-mannose (Ness, Fletcher, and Hudson, *J. Amer. Chem. Soc.*, 1950, **72**, 2200), and that of *N-p*-tolyl-D-xylosylamine tribenzoate gave tribenzoyl D-xylose, identical with that prepared from tribenzoyl xylosyl bromide (Major and Cook, *J. Amer. Chem. Soc.*, 1936, **58**, 2333). Although the structure of this bromide has not been elucidated it is, by analogy with other sugars, presumed to be pyranose: consequently the tribenzoate obtained is 2 : 3 : 4-tribenzoyl D-xylose. This proves that the *N*-arylglycosylamine benzoates examined are pyranoses, so that in benzylation, also, the *N*-arylglycosylamines react as pyranose compounds. The method described for preparing D-glucose and D-mannose tetrabenzoates and D-xylose tribenzoate constitutes the simplest method for obtaining them in high yield. The benzoates of the *N*-arylglycosylamines are considerably more resistant to acid hydrolysis than the acetates.

N-Phenylglucosylamine tetramethyl ether was prepared in several ways. Irvine and Gilmour (*J.*, 1908, **93**, 1429) have prepared the α -pyranose compound, $[\alpha]_D +238^\circ \longrightarrow +47^\circ$ (in methanol containing a trace of hydrochloric acid), by methylating *N*-phenylglucosylamine with methyl iodide-silver oxide and by condensation of aniline and 2 : 3 : 4 : 6-tetramethyl D-glucose at room temperature. Irvine and Moody (*J.*, 1908, **93**, 95) and Pringsheim and Steingröver (*Ber.*, 1926, **59**, 1001) obtained the same compound by boiling the reagents in ethanol. Both methods of condensation were repeated in the present work, and, in addition, *N*-phenylglucosylamine was methylated by a modification of Haworth's method. All three gave, as the only product, the α -anomer. The yield by the last method, however, was low, as expected from the susceptibility of *N*-phenylglucosylamine to alkali. The same ether was also prepared from tetramethyl D-glucopyranosyl bromide and aniline, although, by analogy with the acetate, the β -anomer was expected. The mutarotation of *N*-phenylglucosylamine 2 : 3 : 4 : 6-tetramethyl ether was observed in pure methanol: this mutarotation cannot involve pyranose-furanose change. No mutarotation was observed in acetone or in chloroform. On leaving a methanol solution of the ether which had reached equilibrium, $[\alpha]_D +47^\circ$, to evaporate at room temperature, *N*-phenyl- α -D-glucosylamine 2 : 3 : 4 : 6-tetramethyl ether, $[\alpha]_D +217^\circ$ (initial value in methanol), was obtained. The isomerization during mutarotation had thus been reversed during the slow evaporation. The condensation of *p*-toluidine and tetramethyl D-glucose in cold ethanol gave the same product as from condensation in boiling ethanol, or in low yield by methylation of *N-p*-tolyl-D-glucosylamine (Kuhn and Dansi, *loc. cit.*). The physical constants of the specimen, m. p. 151—152°, $[\alpha]_D^{17} +221.4^\circ \longrightarrow +60.0^\circ$ (*c*, 0.5 in methanol), $[\alpha]_D^{16} +207.0^\circ$ (*c*, 1.0 in chloroform), obtained from the condensation at room temperature are noticeably higher than those previously recorded. The low yield of tetramethyl ether obtained by methylation of *N*-phenyl- and of *N-p*-tolyl-D-glucosylamine made this method of little value for investigating structures and hence its application to other glycosides was not pursued.

All the derivatives of the *N*-arylglycosylamines described in this paper are pyranose. Under diverse conditions the *N*-arylglycosylamines react in the pyranose form and no valid evidence has yet been presented for the existence of a furanose isomer. The composition of the equilibrium mixture which exists in solution has not yet been studied in detail but the similarity of behaviour of these compounds in certain respects to the aldoses themselves is striking.

EXPERIMENTAL

M. p.s are uncorrected. All solvents used for measurements of specific rotations were purified to remove moisture. The light petroleum used had b. p. 60—80°.

Acetylation of N-p-Tolyl- β -D-glucosylamine.—A solution of *N-p*-tolyl- β -D-glucosylamine (3 g., 1 mol.) in pyridine (30 ml.) containing acetic anhydride (4.4 ml., 1 mol.) was kept at -5°

for 30 minutes and then at 0° for 36 hours. The crude product (4.2 g., 85%), obtained by precipitation with ice-water, crystallized from ethanol to give *N-p*-tolyl-β-D-glucosylamine 2 : 3 : 4 : 6-tetra-acetate, m. p. 141—143°, $[\alpha]_D^{20} - 32.7^\circ$ (c, 0.6 in chloroform). Honeyman and Tatchell (*loc. cit.*) record m. p. 144—145°, $[\alpha]_D^{18} - 33.4^\circ$ (c, 0.4 in chloroform).

Hydrolysis of N-p-Tolyl-β-D-glucosylamine Tetra-acetate.—The procedure followed was that described by Butler *et al.* (*loc. cit.*). From *N-p*-tolylglucosylamine tetra-acetate (2 g.) crystals were obtained, m. p. 122—124° (1.5 g., 94%), which were recrystallized from acetone-ether-light petroleum to give 2 : 3 : 4 : 6-tetra-acetyl D-glucose, m. p. 124—126°, $[\alpha]_D^{17} + 31.6^\circ$ (c, 0.5 in chloroform), $[\alpha]_D^{17} + 31.6^\circ \rightarrow +36.7^\circ$ (c, 0.5 in chloroform containing a trace of ethanol). For this compound Hendricks, Wulf, and Liddell (*loc. cit.*) give constants including m. p. 120—120.5°, $[\alpha]_D + 30^\circ$ (in ethanol).

Condensations with Tetra-acetyl D-Glucopyranose.—(a) A solution of 2 : 3 : 4 : 6-tetra-acetyl D-glucose (3 g., 1 mol.) and aniline (0.8 g., 1 mol.) in absolute ethanol (30 ml.) was refluxed for 2 hours. The solvent was removed and there separated crude crystals (1.6 g., 44%) which on recrystallization from ethanol gave *N*-phenyl-α-D-glucosylamine 2 : 3 : 4 : 6-tetra-acetate, m. p. 146—148°, $[\alpha]_D^{19} + 178.9^\circ$ (c, 0.4 in chloroform). Honeyman and Tatchell give m. p. 149—150°, $[\alpha]_D^{16} + 180^\circ$ (c, 2.5 in chloroform). (b) A solution of 2 : 3 : 4 : 6-tetra-acetyl D-glucose (1 g., 1 mol.) in ethanol (20 ml.) was refluxed with *p*-toluidine (0.3 g., 1 mol.) for 2 hours. After isolation as in (a), the crude crystals (1.0 g., 83%) were recrystallized from methanol, to give *N-p*-tolyl-β-D-glucosylamine 2 : 3 : 4 : 6-tetra-acetate, m. p. 141—142°, $[\alpha]_D^{21} - 35.0^\circ$ (c, 0.6 in chloroform). Honeyman and Tatchell record m. p. 144—145°, $[\alpha]_D^{18} - 33.4^\circ$ (c, 0.4 in chloroform).

Condensations with 2 : 3 : 4 : 6-Tetra-acetyl D-Glucosyl Bromide.—(i) A mixture of tetra-acetyl D-glucosyl bromide (5 g., 1 mol.), *p*-toluidine (1.3 g., 2 mol.), and mercuric acetate (1 g., 0.5 mol.) was warmed to 60° for 15 minutes. The solution became dark brown and resinous and no solid product was obtained.

(ii) A solution of the bromide (2.5 g., 1 mol.), *p*-toluidine (0.6 g., 2 mol.), and mercuric acetate (0.5 g., 0.5 mol.) was made in sodium-dried ether (25 ml.) and left at room temperature for 9 hours. The filtrate was washed, dried, and evaporated, leaving a syrup which gave a small amount of solid, $[\alpha]_D + 70.6^\circ$ (c, 0.2 in chloroform), which was not identified.

(iii) The directions of (ii) were followed but the reaction time was 2 hours at room temperature followed by 4 hours at 0°. Crystals of *N-p*-tolyl-β-D-glucosylamine 2 : 3 : 4 : 6-tetra-acetate, m. p. 140°, $[\alpha]_D^{20} - 33.1^\circ$ (c, 0.5 in chloroform), were obtained.

(iv) The preceding experiment was repeated with a higher proportion of mercuric acetate (2 g., 1.6 mol.). The product was the same tetra-acetate.

N-p-Tolyl-D-glucosylamine Tetrabenzoate.—Benzoyl chloride (12 ml., 8 mol.) in pyridine (8 ml.) was added slowly to a solution of *N-p*-tolylglucosylamine (3.5 g., 1 mol.) in pyridine (5 ml.) while the temperature was kept at 0°. After 3½ hours at 0° the reaction mixture was poured into water. The oil which separated was washed thoroughly with cold water and then triturated with ethanol. Recrystallization from acetone-ethanol yielded *N-p*-tolyl-D-glucosylamine 2 : 3 : 4 : 6-tetrabenzoate, m. p. 209°, $[\alpha]_D^{15} + 14.1^\circ$ (c, 0.4 in chloroform), $[\alpha]_D^{19} + 50.0^\circ$ (c, 0.4 in benzene) (Found : C, 71.3; H, 5.1; N, 2.3. C₄₁H₃₅O₉N requires C, 71.8; H, 5.1; N, 2.1%).

N-p-Tolyl-D-mannosylamine Tetrabenzoate.—A solution of *N-p*-tolylmannosylamine (1.5 g., 1 mol.) was made by heating it to ca. 70° in pyridine (12 ml.). When solution was complete, it was rapidly cooled to 0° and benzoyl chloride (1.1 ml., 5 mol.) in pyridine (2 ml.) was dropped into it. The reaction mixture was left at 0° for 2 hours before being poured into ice-water. The white paste, after repeated washing with water, was dissolved in chloroform and the solution washed several times with 5*N*-hydrochloric acid, with 1% sodium carbonate solution, and with water. The syrup obtained after drying, filtration, and evaporation crystallized under methanol. This crude product (2.8 g., 74%), recrystallized from methanol-light petroleum, was *N-p*-tolyl-D-mannosylamine 2 : 3 : 4 : 6-tetrabenzoate, m. p. 133—134°, $[\alpha]_D^{14} - 125.6^\circ$ (c, 0.8 in chloroform) (Found : C, 71.9; H, 5.1; N, 2.2. C₄₁H₃₅O₉N requires C, 71.8; H, 5.1; N, 2.1%).

N-p-Tolyl-D-xylosylamine Tribenzoate.—Benzoyl chloride (0.8 ml., 3.5 mol.) was dropped into a solution of *N-p*-tolyl-D-xylosylamine (0.5 g., 1 mol.) in pyridine (8 ml.) kept at 0°. The mixture was left at 0° for 15 minutes and then poured into well-stirred ice-water. The white paste, treated as described in the previous experiment, yielded crude crystals (2.0 g., 86%) which were recrystallized from ethanol, giving *N-p*-tolyl-D-xylosylamine 2 : 3 : 4-tribenzoate, m. p. 180—181°, $[\alpha]_D^{22} + 48.3^\circ$ (c, 0.6 in chloroform) (Found : C, 72.1; H, 5.5; N, 2.8. C₃₅H₂₉O₇N requires C, 71.9; H, 5.3; N, 2.5%).

Benzoylation of N-Phenylglucosylamine.—Attempts to benzoylate *N*-phenyl-D-glucosylamine (1 mol.) with benzoyl chloride (5 mol.) in pyridine at 0° for reaction times varying from 15 minutes to 3 hours, gave, each time, benzanilide, identified by m. p. and mixed m. p. 159—160°, $[\alpha]_D \pm 0^\circ$ (in chloroform), as the only solid product.

Benzoylation of N-Phenyl-D-ribosylamine.—Benzanilide was also obtained on treatment of *N*-phenyl-D-ribosylamine B (1 mol.) in pyridine with benzoyl chloride (4 mol.) at 0° for 10—90 minutes or at –18° for 20 minutes.

Hydrolysis of N-p-Tolyl-D-glucosylamine Tetrabenzoate.—(a) The method used for removing the amine group of acetates (see above) was tried, but, after 5 hours' refluxing, unchanged material was recovered.

(b) A solution of *N*-p-tolyl-D-glucosylamine tetrabenzoate (1 g.) in acetone (25 ml.) was boiled under reflux with dilute hydrochloric acid (2 ml. of concentrated acid in 25 ml. of water) for 5 hours. The acetone was distilled off and the aqueous solution was extracted with chloroform. The extract was washed with water, dried, filtered, and evaporated, leaving crystals (0.7 g., 80%). Recrystallization from ethanol–light petroleum gave 2 : 3 : 4 : 6-tetrabenzoyl D-glucose, m. p. 114—116°, $[\alpha]_D^{18} + 90.1^\circ$ (c, 0.2 in chloroform), $[\alpha]_D^{18} + 73.4^\circ$ (c, 0.4 in ethanol). Fischer and Noth (*loc. cit.*) record m. p. 119—120°, $[\alpha]_D^{19} + 70.6^\circ$ (c, 5.0 in ethanol), for this compound.

Hydrolysis of N-p-Tolyl-D-mannosylamine Tetrabenzoate.—This compound (1 g.) was boiled with acetone (50 ml.), water (25 ml.), and concentrated hydrochloric acid (2 ml.) for an hour. The product, isolated as in the above preparation, was recrystallized from ethanol to give mannose 2 : 3 : 4 : 6-tetrabenzoate (0.5 g., 60%), $[\alpha]_D^{18} - 88^\circ$ (c, 0.5 in chloroform) and m. p. 178—179°, undepressed on admixture with an authentic sample, m. p. 182—184°, supplied by Dr. H. G. Fletcher {Ness, Fletcher, and Hudson, *loc. cit.*, record m. p. 182—184°, $[\alpha]_D^{20} - 82.6^\circ$ (c, 1.04 in chloroform)}.

Hydrolysis of N-p-Tolyl-D-xylosylamine Tribenzoate.—This compound (1 g.), hydrolysed as above, gave crystals (0.6 g., 76%) which were recrystallized from ethanol and then from benzene. The product was xylose 2 : 3 : 4-tribenzoate, m. p. 183—184°, undepressed on admixture with a sample, $[\alpha]_D^{19} + 25.5^\circ$ (c, 2.0 in chloroform), m. p. 181—183°, prepared by Major and Cook's method, and supplied by Dr. H. G. Fletcher (Found: C, 67.4; H, 4.4. Calc. for $C_{28}H_{22}O_8$: C, 67.5; H, 4.8%). Major and Cook (*loc. cit.*) record for xylose tribenzoate, m. p. 188—189°, $[\alpha]_D^{20} + 39.5^\circ$ (c, 2 in chloroform).

N-Phenyl-D-glucosylamine Tetramethyl Ether.—(i) (cf. Irvine and Moody, *loc. cit.*; Pringsheim and Steingröver, *loc. cit.*). A solution of 2 : 3 : 4 : 6-tetramethyl D-glucose (7 g., 1 mol.) in ethanol (15 ml.) was refluxed with aniline (7 g., 2.3 mol.) for 4 hours. The cooled solution, which contained crystals, was steam-distilled for 15 minutes. The crude crystals (8.1 g., 88%) which remained were identified after recrystallization from aqueous ethanol as *N*-phenyl- α -D-glucosylamine 2 : 3 : 4 : 6-tetramethyl ether, m. p. 133—135°, $[\alpha]_D^{18} + 227.8^\circ \rightarrow +57.5^\circ$ (c, 1.6 in methanol).

(ii) A solution of 2 : 3 : 4 : 6-tetramethyl D-glucose (3 g., 1 mol.) in ethanol (8 ml.) containing aniline (3 g., 2.3 mol.) was kept at room temperature for 2 days. The crystals (2.8 g., 71%) obtained had m. p. 134—135°, $[\alpha]_D^{18} + 224.3^\circ \rightarrow +65.5^\circ$ (c, 1.8 in methanol), $[\alpha]_D^{18} + 240.0^\circ$ (c, 1.1 in acetone), $[\alpha]_D^{18} + 238.8^\circ$ (c, 0.6 in chloroform), and were identical with those from (i).

(iii) Tetramethyl D-glucose (2.4 g., 1 mol.) was converted into tetramethyl-D-glucopyranosyl bromide (which was not isolated) by Wolfrom and Husted's method (*J. Amer. Chem. Soc.*, 1937, 59, 2559). The bromide was dissolved in chloroform containing aniline (3 ml., 3 mol.) and kept in the refrigerator for 10 days. Steam-distillation left crude crystals (0.7 g., 23%) of *N*-phenyl- α -D-glucosylamine 2 : 3 : 4 : 6-tetramethyl ether, m. p. 112—127°, $[\alpha]_D^{18} + 190^\circ$ (c, 0.9 in acetone).

(iv) A solution of *N*-phenylglucosylamine (5 g., 1 mol.) in warm water (30 ml.) was methylated under mild conditions with methyl sulphate (92 ml., 40 mol.) and sodium hydroxide solution (26%). The reaction was started at room temperature by slowly dropping in equal quantities of methyl sulphate and sodium hydroxide solution. After 45 minutes the temperature was raised to 30° and then to 40° during the following 2 hours. The addition of reagents was completed in 5 hours and the temperature was slowly raised to 50—55° for an hour. On cooling, the reaction mixture was diluted with water and extracted with chloroform. The extract, after being washed with water, dried, and filtered, was evaporated and gave crude crystals (1.3 g., 25%) which were recrystallized from ethanol, to yield *N*-phenyl- α -D-glucosylamine 2 : 3 : 4 : 6-tetramethyl ether, m. p. 133—135°, $[\alpha]_D^{18} + 206.3^\circ$ (c, 1.0 in chloroform).

Mutarotation. A solution of this compound, m. p. 133—135°, $[\alpha]_D^{18} + 227.8^\circ$ (initial value) in methanol (25 ml.) was kept until its specific rotation was constant. The solution, allowed to

evaporate slowly at room temperature, deposited colourless needles, m. p. 130—135°, $[\alpha]_D^{15} +217.0^\circ$ (*c*, 0.5 in methanol, initial value).

N-p-Tolylglucosylamine 2:3:4:6-Tetramethyl Ether.—(i) A solution of 2:3:4:6-tetramethyl D-glucose (3 g., 1 mol.) and *p*-toluidine (3 g., 1.2 mol.) in ethanol (12 ml.) was left at room temperature for 7 days. The precipitated crystals (3.7 g., 89%) were recrystallized from ethanol to give *N-p*-tolylglucosylamine 2:3:4:6-tetramethyl ether, m. p. 151—152°, $[\alpha]_D^{17} +221.4^\circ \longrightarrow +60.0^\circ$ (*c*, 0.5 in methanol), $[\alpha]_D^{16} +207.0^\circ$ (*c*, 1.0 in chloroform). Irvine and Hynd (*J.*, 1911, **99**, 161) record for this compound m. p. 144°, $[\alpha]_D^{20} +156.5^\circ \longrightarrow +53.5^\circ$ (*c*, 1.1 in methanol).

(ii) *N-p*-Tolylglucosylamine (5 g., 1 mol.) was methylated in the way described for *N*-phenylglucosylamine above. The product (2 g., 33%) was the 2:3:4:6-tetramethyl ether, m. p. 143—144°, $[\alpha]_D^{19} +200.0^\circ \longrightarrow +58.8^\circ$ (*c*, 0.2 in methanol). Kuhn and Dansi give m. p. 147—150°, $[\alpha]_D +163^\circ$ (initial value in methanol).

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KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON, W.C.2.

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