## 436. *Nitrogen-containing Carbohydrate Derivatives. Part II.*[1] *Methyl 4,6-O-Benzylidene-3-deoxy-3-phenylazo-α-D-glucoside: Configuration, Reduction, and Irradiation.*

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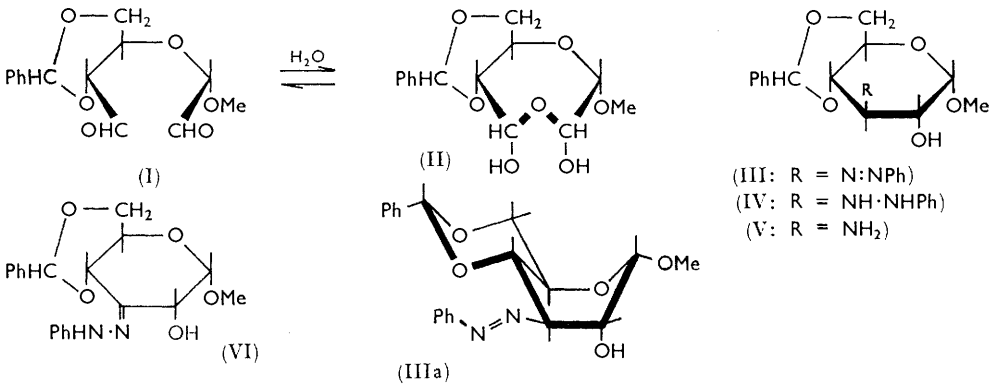
The configuration of the phenylazo-compound (III), named in the title, has been proved by conversion into the phenylhydrazino- (IV) and thence into the amino-analogue (V). Its preparation in the dark has led to isolation of the *trans*-azo-form, which on irradiation changes to a stereoisomeric form; this is believed to be conformational rather than *trans–cis*-isomerism. Reduction of the phenylazo-compound (III) by a number of reagents has been compared with that of arylazoarenes; the N–N link in the phenylhydrazino-compound (IV) seems particularly resistant to cleavage. The mechanism of the formation of compound (III) is discussed in the light of recent work on the rearrangement of alkyl phenylhydrazones.

IN Part I [1] it was established chemically that the product (A) of reaction of aqueous phenylhydrazine with periodate-oxidised methyl 4,6-*O*-benzylidene-α-D-glucoside [in whose aqueous solutions an equilibrium exists between the dialdehyde (I) and the hemialdal (II) [2-4]] was a methyl 4,6-*O*-benzylidene-3-deoxy-3-phenylazo-α-D-hexoside of either the *gluco*- (III) or the *allo*-configuration. The basic structure was proved by proton magnetic resonance studies [1,5] which, when extended to the derived 2-acetate, led to the assignment of the *gluco*-configuration (III).[1] Hydrogenation of the phenylazo-compound (III) in ethanol with Raney nickel to methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-glucoside (V) was not considered in our earlier work as evidence that the product (A) had the *gluco*-configuration because tautomeric change to the phenylhydrazone (VI) during the reduction was a possibility. Also there was some confusion in the literature about the relative stabilities of the hydrazone and the azo-forms of phenylhydrazones; in the aliphatic series the former were apparently the more stable.




However, since then, in a detailed study O'Connor [6] has shown that in neutral solution the phenylhydrazone form (VII) of aliphatic ketones and aldehydes is rapidly converted into the phenylazoalkane (VIII), as shown by the ultraviolet spectra. It appears that the

(VII) $R_2C{:}N{\cdot}NHPh \longrightarrow R_2CH{\cdot}N{:}NPH$ (VIII)

[1] Part I, Guthrie and Johnson, *J.*, 1961, 4166.
[2] Guthrie and Honeyman, *J.*, 1959, 2441.
[3] Guthrie, Honeyman, and Parsons, *J.*, 1959, 2449.
[4] Colbran, Guthrie, and Parsons, *J.*, 1960, 3562.
[5] Turner, *J.*, 1962, 847.
[6] O'Connor, *J. Org. Chem.*, 1961, **26**, 4375.

conversion (VII) ⟶ (VIII) is either an irreversible reaction or that an equilibrium, if in fact involved, lies almost entirely on the side of the azo-isomer. We now therefore assume that under the reduction conditions used [1] the phenylazo-sugar (A) would not rearrange and so will have the same configuration as the resulting 3-amino-sugar (V).

Unaware of O'Connor's work we set out to prove the configuration of the phenylazo-compound (A) by the sequence of reactions (III) ⇄ (IV) ⟶ (V). The lithium aluminium hydride–lead chloride reagent [7] is known to reduce arylazoarenes to hydrazo-compounds: from the yellow phenylazo-compound (A) it produced a colourless methyl 4,6-*O*-benzylidene-3-deoxy-3-phenylhydrazino-α-D-aldohexoside, which was proved to have the *gluco*-configuration (IV) because reduction in the presence of Raney nickel gave methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-glucoside (V); no isomerisation is possible in this reduction. Oxidation of the phenylhydrazino-compound (IV) with a suspension of yellow mercuric oxide in ether [8] gave back the original phenylazo-compound (A) in good yield; since this oxidation involves only the two nitrogen atoms, and not a ring carbon atom, the phenylazo-compound (A) must have the same configuration as both the amino-(V) and the phenylhydrazino-compound (IV), that is *gluco* (III). Thus the result of the proton magnetic resonance studies was confirmed chemically. The phenylhydrazino-compound (IV) was slowly autoxidised to the phenylazo-sugar (III); a sample kept for a year had an infrared spectrum almost identical with that of the phenylazo-sugar.

Photoisomerisation between the *cis*- and the *trans*-forms of arylazoarenes is well known. As the phenylazo-compound (III) was usually prepared under normal lighting conditions, we investigated its configuration and the possibility of photoisomerisation. Azobenzene normally exists in the *trans*-form, but on irradiation an equilibrium mixture containing 15—40% of the *cis*-form is produced.[9] The two forms, which were easily separated on alumina,[10] were both reduced to hydrazobenzene,[11] confirming their stereoisomeric structures. The only apparent reference to the photoisomerisation of arylazoalkanes is by O'Connor and Rosenbrook [12] who irradiated 2-*p*-tolylazobutane to constant spectral values. This was presumed to be a case of *cis–trans*-isomerism because the spectrum did not shift towards that characteristic of a *p*-tolylhydrazone.

Ultraviolet maxima in ethanol.

| | $\pi \longrightarrow \pi^*$ | | $n \longrightarrow \pi^*$ | |
|---|---|---|---|---|
| | $\lambda_{max.}$ | ε | $\lambda_{max.}$ | ε |
| (1) *trans*-Phenylazo-glucoside (*trans*-III) | 266 | 11,700 | 391 | 225 |
| (2) Irradiated (1) | 266 | 11,000 | 398 | 263 |
| (3) *trans*-Phenylazo-glucoside 2-acetate | 267 | 11,200 | 403 | 225 |
| (4) Irradiated (3) | 270 | 13,771 | 400 | 285 |
| (5) " Normal " phenylazo-glucoside 2-*O*-methyl ether | 266 | 10,930 | 393 | 227 |
| (6) Irradiated (5) | 267 | 9750 | 394 | 313 |
| (7) *trans*-Azobenzene * | 319 | 21,300 | 443 | 510 |
| (8) *cis*-Azobenzene * | 281 | 5260 | 432 | 1518 |

* Birnbaum, Linford, and Style, *Trans. Faraday Soc.*, 1953, **49**, 735.

The phenylazo-glucoside (III) has now been prepared in the absence of light, and this product is considered to be the pure *trans*-form, $[\alpha]_D^{21}$ −17·7° (in EtOH); irradiation of its alcoholic solution gave a stereoisomer, $[\alpha]_D^{21}$ +150° (in EtOH). The melting points of the two products, both sharp, were almost the same, though a mixture of the two melted about 20° lower, showing their non-identity. This large depression shows that the irradiated compound is either a pure compound or a mixture of the *trans*-form and its stereoisomer containing a large proportion of the latter. The stereoisomeric relationship

[7] Olah, *J. Amer. Chem. Soc.*, 1959, **81**, 3165.
[8] Tafel, *Ber.*, 1885, **18**, 1739; Fischer, *Ber.*, 1896, **29**, 794.
[9] Hartley, *J.*, 1938, 633.
[10] Cook, *J.*, 1938, 876.
[11] Cook and Jones, *J.*, 1939, 1309.
[12] O'Connor and Rosenbrook, *J. Org. Chem.*, 1961, **26**, 5208.

was proved by reduction of both compounds to the phenylhydrazino-glucoside (IV) in excellent yield. The irradiation product was stable in boiling ethanol, the rotation falling only slightly during 10 hr.; however, recrystallisation from aqueous ethanol gave a product with $[\alpha]_D^{21}$ +13·3° (in EtOH). The $[\alpha]_D$ values showed that the "normal" phenylazo-glucoside, which had $[\alpha]_D^{21}$ −3·3° (in EtOH), was not the pure *trans*-form. The ultraviolet maxima for the *trans*- and the irradiated form are shown in the Table.

Similar results were obtained with methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-3-phenylazo-α-D-glucoside. Acetylation of the *trans*-phenylazo-glucoside in the dark gave what is assumed to be the pure *trans*-phenylazo-glucoside 2-acetate ($[\alpha]_D^{21}$ +57·4° in MeOH), solutions of which, when irradiated, had $[\alpha]_D^{21}$ +196°. Treatment of both solutions with hydrazine hydrate (see below) both reduced the phenylazo-group to phenylhydrazino and also removed the acetate group,[13] giving in both cases the phenylhydrazino-compound (IV). Thus the *trans*- and the irradiated form were again stereoisomeric. In contrast to the unacetylated compound, the irradiated acetate could not be isolated from its solutions; the material isolated had a specific rotation near to that of the "normal" acetate. The latter compound was again not the pure *trans*-form as it had $[\alpha]_D^{21}$ +63·8° (in MeOH).

Methyl 4,6-*O*-benzylidene-3-deoxy-2-*O*-methyl-3-phenylazo-α-D-glucoside also showed a large upward rotational change on irradiation; no attempts were made to study the product.

The above irradiation experiments could be explained in two ways: (i) normal *trans*- ⟶ *cis*-isomerisation of an azo-group and (ii) change to a more unstable conformation of the pyranose ring, with the azo-group still in the *trans*-configuration. The latter theory is favoured for the following reasons.

The two forms of azobenzene have different ultraviolet spectra (see Table); so have those of other arylazoarenes and similar molecules such as stilbene. The spectra of *cis*- and *trans*-arylazoarenes are different because in the former the chromophore is twisted from co-planarity. Many other examples [14] occur of the alteration of ultraviolet spectra with increased steric hindrance in the chromophoric group. Models of *cis*-phenylazo-glucoside (*cis*-III) showed that its formation would be extremely difficult, if not impossible, if the −N=NPh group was kept co-planar. In the *trans*-form co-planarity is possible, the *trans*-N=N-group holding the phenyl ring well away from the sugar ring. However, the ultraviolet spectra of the *trans*- and the irradiated compound are almost identical, suggesting that the chromophoric group in fact stays co-planar and, therefore, that the irradiated form is not the *cis*-isomer. That the irradiated product was a mixture of *trans*- and a little *cis*-form is ruled out by the melting behaviour described above, and, probably, by the large rotational change on irradiation.

If the irradiated *trans*-phenylazo-glucoside does not lose the energy gained on irradiation by conversion into the more unstable *cis*-form, it could lose it by change of the pyranose ring bearing the chromophore from a chair to an unstable non-chair conformation such as (IIIa), the azo-linkage remaining *trans*. Such a change explains the ultraviolet spectra, and also, it is believed, the large changes in specific rotation. The large difference in molecular rotation between methyl 4,6-*O*-benzylidene-α-D-mannoside and its 2,3-carbonate was believed to be due to the change from a chair conformation in the former to a boat in the latter.[15]

It is also interesting that attempts to separate the *trans*- and the irradiated form after brief irradiation of the phenylazo-glucoside (to $[\alpha]_D$ +70·6°) gave only one product, with a rotation the same as that of the starting material. If our theory is correct, this indicates that the briefly irradiated substance was a single compound with a conformation

[13] Ennor and Honeyman, *J.*, 1958, 2586.
[14] See, *e.g.*, Gillam and Stern, "Electronic Absorption Spectroscopy," Arnold Ltd., 1957, p. 266; Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890.
[15] Hough and Priddle, *J.*, 1961, 3178.

whose stability was between that of the *trans*-form and the final irradiation product of $[\alpha]_D^{21}$ +150°. It is hoped that work on simpler systems will clarify the issues.

The difference in stability between the irradiated unacetylated and the irradiated acetylated phenylazo-glucoside is believed to be due to hydrogen bonding. The former compound can form a hydrogen bond between the 2-hydroxyl group and the nitrogen atom β to the pyranose ring in the *trans*-chair, -skew, or -boat ($B_1E$) [16] conformation; the acetate cannot, so it reverts to the most stable form when the energy source is removed.

Several reducing agents have been tried for reduction of the phenylazo- (III) to the amino-sugar derivative (V), and also for a comparison of the reactions of arylazoalkanes with those of arylazoarenes; the former class of azo-compounds has been neglected and comparatively few references occur to their chemistry.[17] The reactions mentioned previously, catalytic hydrogenation with Raney nickel [1] and reduction by lithium aluminium hydride–lead chloride, occurred in the same way as with arylazoarenes, giving amino- and hydrazino-compounds, respectively. It was previously reported [1] that the phenylazo-compound (III) was catalytically reduced to the amino-sugar (IV) in presence of platinum oxide. Further work has shown that this is an unreliable method as the second stage of the reduction [N–N cleavage of the hydrazino-derivative (IV)] depends critically on the activity of the catalyst. This agrees with work by Strel'tsova and Zelinskii [18] with azobenzene. They also reported that hydrogenation with a palladium catalyst smoothly reduced azobenzene to aniline. We have repeated this result but, with the same batch of catalyst, the phenylazo-compound (III) was reduced only to the phenylhydrazino-derivative.

We next examined hydrazine hydrate in the presence of various metal catalysts. Bavin [19] and Pietra [20] have reported that azobenzene was thus reduced to hydrazobenzene with palladium–charcoal and, more slowly, to aniline in good yield.[20] The latter result was not obtained by us, hydrazobenzene being formed in good yield whatever the reaction time. From the phenylazo-sugar (III) this reagent gave the phenylhydrazino-derivative in good yield. Reduction of azobenzene with hydrazine hydrate and Raney nickel gave hydrazobenzene or aniline depending on the excess of the reagent used. However, even with a large excess of hydrazine hydrate (80 mol.) the phenylazo-sugar only gave the phenylhydrazino-compound. Pietra [20] reported that platinum–charcoal gave the same results as a palladium catalyst, although elsewhere [21] it is stated that this reagent reduced azobenzene to hydrazobenzene. With the phenylazo-sugar the same result was obtained as with the other catalysts.

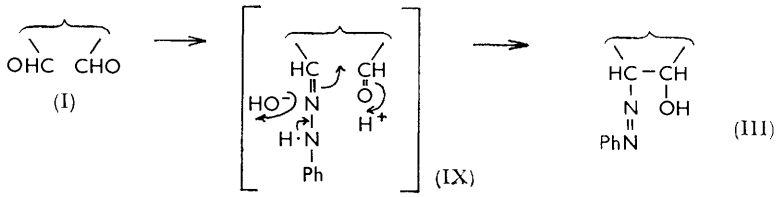
Sodium dithionite, a reducing agent widely used for cleaving aromatic azo-compounds, particularly dyes, reduced the phenylazo-glucoside (III) only to the phenylhydrazino-derivative, even when a great excess (7 mol.) was used. It is interesting that arylazoarenes with strongly deactivating groups, such as phenylsulphonyl, are reduced by this reagent only to the arylhydrazino-arene.[22]

It has been reported,[23] with mention of only brief practical details and no examples, that thiourea dioxide (aminoiminomethanesulphinic acid) cleaves azo- and hydrazino-compounds to amines. However, we have found that azobenzene and the phenylazo-sugar (III) were thus reduced only to the hydrazino-compounds under conditions used for reduction of disulphides.[24]

[16] Isbell and Tipson, *J. Res. Nat. Bur. Stand.*, 1960, **64**, *A*, 171.
[17] Zollinger, "Azo and Diazo Chemistry," Interscience Publ., Inc., New York, 1961.
[18] Strel'tsova and Zelinskii, *Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim.*, 1941, 401; *Chem. Abs.*, 1942, **36**, 418.
[19] Bavin, *Canad. J. Chem.*, 1958, **36**, 238.
[20] Pietra, *Ann. Chim. (Italy)*, 1957, **47**, 410.
[21] Stafford, Los, and Thompson, *Chem. and Ind.*, 1956, 1277.
[22] Bradley and Hannon, *J.*, 1962, 2713; Pearl, *J. Org. Chem.*, 1945, **10**, 205.
[23] Gore, *Chem. and Ind.*, 1954, 1355.
[24] Takagi, Tanaka, and Yokoyama, *Pharm. Bull. (Tokyo)*, 1957, **5**, 615; *Chem. Abs.*, 1958, **52**, 6,189.

Thus, if methyl 4,6-*O*-benzylidene-3-deoxy-3-phenylazo-α-D-glucoside (III) is a typical arylazoalkane, it appears that this class of compound readily undergoes reduction to the hydrazino-stage, but that reductive cleavage of the N–N bond occurs much less readily than with the fully aromatic analogues.

Reduction of the phenylazo-sugar (III) with methanolic potassium borohydride gave a mixture which appears to be derived from the dialdehyde monophenylhydrazone (IX);[25] the structures of these products have not yet been fully elucidated.




O'Connor's findings[6] add further support to the mechanism proposed[1] for the formation of the phenylazo-sugar (III) through the phenylhydrazone intermediate (IX), the driving force for the reaction coming from the rearrangement of the phenylhydrazone group with subsequent carbon–carbon bond formation. O'Connor *et al.*[12] also showed that *p*-nitrophenylhydrazones of aliphatic ketones and aldehydes were stable under conditions where the corresponding phenylhydrazones rearranged because of the presence of the deactivating nitro-group. They also found that the corresponding *p*-tolylhydrazones readily rearranged to *p*-tolylazoalkanes. These findings also support our mechanism since it has been shown that the dialdehyde (I) with *p*-nitrophenylhydrazine gave only a bisarylhydrazone,[4] but with *p*-tolylhydrazine gave methyl 4,6-*O*-benzylidene-3-deoxy-3-*p*-tolylazo-α-D-glucoside.[25]

## Experimental

Paper chromatography was on Whatman No. 1 paper with butan-1-ol–ethanol–water (40 : 19 : 11) followed by spraying with ninhydrin. Hydrazine hydrate was 99—100% material. Compounds were identified by mixed m. p. and comparison of infrared spectra. Solvents were removed *in vacuo*.

*Reduction of Methyl* 4,6-O-*Benzylidene*-3-*deoxy*-3-*phenylazo*-α-D-*glucoside* (III).—(*a*) *With lithium aluminium hydride.* A solution of the phenylazo-glucoside (1 g.) in ether (100 ml.) was added to a stirred suspension of lithium aluminium hydride (1 g.) in ether (150 ml.) during 6 min. Lead chloride (0·0076 g.) was then added and stirring continued for a further 30 min. The excess of reagent was destroyed with wet ethyl acetate. The aqueous layer was extracted with ether, the extract combined with the main ether layer, and the whole dried ($CaCl_2$). Evaporation of the solvent gave a white solid (0·7 g.), m. p. 151°, which when recrystallised from methanol saturated with sulphur dioxide gave *methyl* 4,6-O-*benzylidene*-3-*deoxy*-3-*phenylhydrazino*-α-D-*glucoside* (IV), m. p. 152·5—153·5°, $[\alpha]_D^{18}$ +94·9° (*c* 1·02 in $CHCl_3$), $R_F$ 0·81, $\lambda_{max.}$ 240, 287, and 394 mμ (ε 10,750, 1850, and 128, respectively, in EtOH) (Found: C, 64·4; H, 6·5; N, 7·6. $C_{20}H_{24}N_2O_5$ requires C, 64·5; H, 6·5; N, 7·6%). The product became yellow on exposure to the air; after 1 year a sample had m. p. 162—170° and an infrared spectrum almost identical with that of the phenylazo-sugar (III).

Reduction without addition of lead chloride failed to yield any phenylhydrazino-sugar, even after 3 hr., the only material isolated being unchanged starting compound (96%).

Reduction of the phenylhydrazino-sugar as previously described[1] for the corresponding phenylazo-derivative gave, after recrystallisation from chloroform–light petroleum, methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-glucoside (V) (75%), m. p. 186°, characterised as the 3-acetamido-derivative.

The phenylhydrazino-sugar with acetic anhydride–pyridine for 12 hr. at 0° gave an off-white solid, m. p. 75—80°. No solvent system could be found for recrystallisation of this substance; all those tried gave oils.

[25] Guthrie, unpublished results.

(*b*) *With sodium dithionite.* To a solution of the phenylazo-compound (III) (4 g.) in ethanol (80 ml.) and water (20 ml.) at 70—80° was added, with stirring, sodium dithionite (4 g.) and sodium hydroxide (0·25 g.). The mixture was kept at this temperature for a further 5 hr. during which further sodium dithionite (14 g.) was added in portions (2 g.). Pouring the almost colourless mixture into ice–water (500 ml.) precipitated a white solid (3·8 g.), m. p. 141°, which was washed with water and dried *in vacuo* ($P_2O_5$). Recrystallisation from methanol saturated with sulphur dioxide gave the 3-phenylhydrazino-glucoside (IV) (3·5 g., 85%), m. p. 152—153°.

(*c*) *With thiourea dioxide* (cf. ref. 24). A solution of the phenylazo-glucoside (III) (1 g.) in 50% aqueous *NN*-dimethylformamide (25 ml.) was heated at 70° for 2 hr. with freshly prepared thiourea dioxide,[26] m. p. 128—129° (1 g.), and sodium hydroxide (2 g.). Pouring the colourless solution into ice–water (100 ml.) gave a white solid (0·52 g.), m. p. 140°. Recrystallisation as described above gave the phenylhydrazino-compound, m. p. 148°.

(*d*) *With hydrazine hydrate and Raney nickel.* (i) A solution of the phenylazo-glucoside (1 g.) in ethanol (60 ml.) was boiled under reflux with hydrazine hydrate (2 g.) in the presence of Raney nickel until the yellow colour had disappeared (7 hr.). The solution was filtered through "Celite" and poured into ice–water, to give a white solid (0·68 g.), m. p. 140—142°. Recrystallisation as described above gave the phenylhydrazino-compound, m. p. 148—150°.

(ii) The same reduction with hydrazine hydrate (12·0 g., 80 mol.) gave a colourless solution which rapidly became brown. Working up as above gave a light brown solid (0·96 g.), m. p. 85—96°. Two recrystallisations from ethanol containing about 1% of hydrazine hydrate gave the phenylhydrazino-glucoside (71%), m. p. 150—152°, characterised by mercuric oxide oxidation (see below) to 3-phenylazo-glucoside (III), m. p. 181—183°. Paper chromatography of the crude mixture gave an intense spot at $R_F$ 0·81, with weaker spots at $R_F$ 0·60 [compound (V) [1]], 0·36, and 0·16.

(*e*) *With hydrazine hydrate and* 10% *palladised charcoal.* Repetition of experiment (*d*, i) with palladised charcoal and a reaction time of 1 hr. gave the phenylhydrazino-glucoside (98%), m. p. 148—150°.

(*f*) *With hydrazine hydrate and* 5% *platinised charcoal.* This also gave the phenylhydrazino-glucoside (57%), m. p. 148—150°.

(*g*) *Hydrogenation with* 10% *palladised charcoal.* The phenylazo-glucoside (0·5 g.) in ethanol (25 ml.) was hydrogenated at room temperature and 3 atm. for 4 hr. in the presence of the catalyst. The colourless solution was evaporated to yield a white solid (0·45 g.), m. p. 143°. Recrystallisation from methanol as in (*d*, ii) gave the phenylhydrazino-glucoside (80%), m. p. 149—150°.

*Oxidation of Methyl* 4,6-O-*Benzylidene*-3-*deoxy*-3-*phenylhydrazino*-α-D-*glucoside* (III).—A suspension of yellow mercuric oxide (5 g.) in a solution of the phenylhydrazino-glucoside (1 g.) in ether or benzene (100 ml.) was stirred at 10—15° for 8 hr. and then kept at room temperature overnight. The inorganic solids were removed and the filtrate was evaporated, to yield methyl 4,6-*O*-benzylidene-3-deoxy-3-phenylazo-α-D-glucoside (III) (0·75 g.), m. p. 183—184°, $[\alpha]_D^{21}$ +8·5° (*c* 1·58 in $CHCl_3$) {lit.,[1] m. p. 182—183°, $[\alpha]_D^{20}$ +8·6° (in $CHCl_3$)}.

*Reduction of Azobenzene.*—(*a*) *With thiourea dioxide.* To a solution of azobenzene (1·0 g.) in 50% aqueous ethanol (50 ml.) containing potassium hydroxide (2·0 g.), was added freshly prepared thiourea dioxide [26] (1·5 g.). The mixture was heated under reflux for 1 hr. to give a colourless solution, which, when poured into ice–water (250 ml.), gave a white flocculent precipitate. This was washed with water and dried *in vacuo* ($P_2O_5$) (m. p. 125—128°). Recrystallisation from ethanol gave hydrazobenzene (99%), m. p. 127—128°.

(*b*) *With hydrazine hydrate and* 10% *palladised charcoal.* To azobenzene (1 g.) in ethanol (100 ml.) was added hydrazine hydrate (1·5 g.) and palladised charcoal (0·01 g.). The mixture, when heated under reflux, went colourless within 10 min.; heating was continued for a further 50 min. The solution was filtered through "Celite" and poured into ice–water (250 ml.), to give a white solid (0·91 g.). Recrystallisation from aqueous ethanol gave hydrazobenzene (84%), m. p. 126—127°.

Heating the reaction mixture under reflux for 2 hr. (cf. Pietra [20]) gave hydrazobenzene (82%), m. p. 126—127°.

(*c*) *With hydrazine hydrate and Raney nickel.* Raney nickel (50 mg.) was added, with

[26] Fischer and Hieber, *Z. anorg. Chem.*, 1953, **271**, 229.

shaking, to a solution of azobenzene (1 g.) in ethanol (25 ml.) containing hydrazine hydrate (4·5 ml.) at $<35°$. More catalyst (*ca.* 50 mg.) was added when the reaction had subsided. After 30 min., when the yellow colour of the solution had been discharged, the mixture was poured into ice–water to yield a white flocculent solid, which was washed with water and dried *in vacuo* ($P_2O_5$). Recrystallisation from aqueous ethanol gave hydrazobenzene (96%), m. p. 125—127°.

Azobenzene (1 g.) in ethanol (25 ml.) with hydrazine hydrate (5 ml.) was heated under reflux in the presence of Raney nickel (0·25 g.) for 2 hr. A further amount of hydrazine hydrate (5 ml.) was then added and heating was continued for a further 3 hr. The mixture was filtered through " Celite " and poured into water to give a straw-coloured solution. The aqueous solution was extracted with ether (4 × 100 ml.), and the extract was dried ($MgSO_4$) and evaporated to yield a brown oil (1·1 g.). Distillation yielded aniline (95%), b. p. 182—184°, $n_D^{22}$ 1·5860 (acetanilide, m. p. 114—114·5°).

*Methyl* 4,6-O-*Benzylidene*-3-*deoxy*-3-trans-*phenylazo*-α-D-*glucoside*.—The reaction between periodate-oxidised methyl 4,6-*O*-benzylidene-α-D-glucoside (5·0 g.) and an aqueous solution of phenylhydrazine hydrochloride (1·75 g.) and an excess of sodium acetate was carried out as described previously,[2] but in a photographic dark room illuminated by a " lime-yellow O.B." (Wratten series) light. The product (85%) was purified by two recrystallisations from a small volume of butan-1-ol, to give the trans-*phenylazo-glucoside* (60%), m. p. 182—184°, $[\alpha]_D^{21}$ −17·7° (*c* 1·0 in EtOH) (Found: C, 64·7; H, 6·0. $C_{20}H_{22}N_2O_5$ requires C, 64·9; H, 6·0%). Ultraviolet maxima are given in the Table.

Reduction of the *trans*-phenylazo-glucoside with hydrazine hydrate–palladised charcoal, as described above, gave methyl 4,6-*O*-benzylidene-3-deoxy-3-phenylhydrazo-α-D-glucoside (IV) (94%), m. p. 148—150°.

The *trans*-phenylazo-glucoside with acetic anhydride–pyridine, in the absence of light as above, gave, after two recrystallisations from ethanol–light petroleum, *methyl* 2-O-*acetyl*-4,6-O-*benzylidene*-3-*deoxy*-3-trans-*phenylazo*-α-D-*glucoside*, m. p. 165—166°, $[\alpha]_D^{21}$ +57·5° (*c* 0·68 in MeOH) (Found: C, 64·3; H, 6·0. $C_{22}H_{24}N_2O_6$ requires C, 64·1; H, 5·9%). Ultraviolet maxima are detailed in the Table.

Reduction of the above acetate with hydrazine hydrate–palladised charcoal, as described above, gave the phenylhydrazino-derivative (IV) (86%), m. p. 149—151°, and thence by oxidation with yellow mercuric oxide for 65 hr., the phenylazo-glucoside (III), m. p. 182—183°.

*Irradiation Experiments*.—Irradiations were carried out at 30—35 cm. distance from a Mazda 3800°K, 40 W, fluorescent tube.

(*a*) *Methyl* 4,6-O-*benzylidene*-3-*deoxy*-3-trans-*phenylazo*-α-D-*glucoside*. A solution of this compound in ethanol was irradiated to constant rotation (*c* 1·0) ($[\alpha]_D^{21}$ −17·7° ⟶ +150° in 38 hr.). Ultraviolet maxima for the irradiated solution are given in the Table. The irradiated solution was evaporated *in vacuo* at 10° to give the *product*, m. p. 185·5—186·5°, $[\alpha]_D^{21}$ +150° (*c* 0·8 in EtOH) (Found: C, 65·0; H, 6·2. $C_{20}H_{22}N_2O_5$ requires C, 64·9; H, 6·0%). A mixed m. p. with the starting compound was 162—170°.

Boiling the product in ethanol under reflux for 10 hr. caused a slight decrease in optical rotation, to $[\alpha]_D^{21}$ +142°.

Recrystallisation from aqueous ethanol gave a product, m. p. 182—184°, $[\alpha]_D^{21}$ +13·3° (*c* 1·06 in EtOH).

Reduction with hydrazine hydrate–palladised charcoal, as described above, gave the phenylhydrazino-compound (IV) (90%), m. p. 148°, and thence by oxidation the " normal " phenylazo-glucoside (69%), m. p. 182°.

The " normal " phenylazo-glucoside (251 mg.) in sodium-dried ether (25 ml.) was irradiated for 15 hr. to give a solution of $[\alpha]_D^{22}$ +70·6°. Chromatography of this solution on alumina gave only one bright yellow product (221 mg.) that had m. p. 183—184°, $[\alpha]_D^{22}$ +66° (*c* 0·94 in EtOH), $[\alpha]_D^{22}$ +67·1° (*c* 0·94 in $Et_2O$); there was no indication of any other components.

(*b*) *Methyl* 2-O-*acetyl*-4,6-O-*benzylidene*-3-*deoxy*-3-trans-*phenylazo*-α-D-*glucoside*. A solution of the acetate in methanol was irradiated to constant specific rotation (*c* 0·68) {$[\alpha]_D^{21}$ +57·4° ⟶ +196° in 38 hr.}. Evaporation *in vacuo* at 10° then gave a yellow solid, m. p. 165—167°, $[\alpha]_D^{22}$ +62° (*c* 0·58 in MeOH). Repetition of the experiment gave a product, m. p. 166°, $[\alpha]_D^{21}$ +59° (*c* 0·61 in MeOH). Ultraviolet maxima for the irradiated solution are shown in the Table.

An irradiated solution of maximum specific rotation was treated with hydrazine hydrate

and palladised charcoal, yielding the phenylhydrazino-glucoside (IV) (86%), m. p. 149—151°, converted by oxidation into the " normal " phenylazo-glucoside (70%), m. p. 182—183°.

(*c*) *Methyl* 4,6-O-*benzylidene*-3-*deoxy*-2-O-*methyl*-3-*phenylazo*-α-D-*glucoside*. A solution of the " normal " compound [1] in ethanol, $[\alpha]_D^{21}$ +67·3° (*c* 1·01), was irradiated to constant rotation (46 hr.), $[\alpha]_D^{21}$ +126°. Ultraviolet maxima are given in the Table.

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