Arylazo-glycenosides. Part II.[1] Additions of Dienes and Dimethylsulphoxonium Methylide to Some 2- and 3-Arylazo-derivatives of Methyl 4,6-*O*-benzylidene-2,3-dideoxy-D-hex-2-enopyranosides

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Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-α-D-hex-2-enopyranoside reacted with dimethylsulphoxonium methylide, by addition of a methylene group to the carbon–carbon double bond of the azoalkene system, to give methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-*C*-methylene-2-phenylazo-α-D-allopyranoside. In contrast, methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-α-D-hex-2-enopyranoside gave, upon treatment with this ylide, a mixture of 1′-phenyl (methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*arabino*- and *ribo*-hexopyranosido [3,2-*c*]-$\Delta^{2'}$-pyrazolines. The β-anomer behaved in like fashion, but only one of the isomeric products was isolated. Support for a structure having fused five- and six-membered rings was obtained by oxidative degradation studies, in which one of the α-isomers was converted into 1-phenylpyrazole-3,4-dicarboxylic acid.

The α-anomers of the 2- and 3-phenylazo-derivatives of methyl 4,6-*O*-benzylidene-2,3-dideoxy-D-hex-2-enopyranoside both form adducts with acrylonitrile and methyl acrylate, and the α-anomer of the 3-phenylazo-derivative has been shown to give an adduct with dimethylacetylene dicarboxylate.

In the preceding paper[1] we showed that methyl 4,6-*O*-benzylidene-2,3-dideoxy-phenylazo-D-hex-2-enopyranosides could be prepared in high yields and that these derivatives undergo 1,4-addition reactions with a wide range of nucleophiles. Now we report further reactions of these compounds, with reagents that lead to 2,3-annulation products.[2]

As we have pointed out[1] there is a similarity between the reactions of azoalkenes and conjugated enones. Consequently, it appeared of interest to examine the behaviour of these carbohydrate azoalkene derivatives with dimethylsulphoxonium methylide, since by analogy with the reaction of this ylide with conjugated ketones a cyclopropane derivative would be expected.[3] Such a reaction seemed especially worthy of study because of recent interest[4-6] in cyclopropane carbohydrate derivatives.

Treatment of the methyl 2-phenylazo-α-D-*erythro*-hex-2-enopyranoside (1) with dimethylsulphoxonium methylide afforded a yellow solid which was shown to be the cyclopropane derivative (2). Its structure was deduced from the molecular formula (elemental analysis and the molecular ion, *m/e* 366), the u.v. absorption maximum at 278 nm, and the yellow colour (indicative of a phenylazo-residue), and the i.r. and n.m.r. spectra. All the proton signals expected for a derivative with the proposed structure were observed and their assignments were verified by double-resonance experiments (see Table 1). Particularly relevant are the three discrete signals at high field which are indicative of three hydrogen atoms attached to a cyclopropane ring. This product is closely related to methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-*C*-methylene-α-D-allopyranoside, which has been prepared by two independent routes.[4,5] A comparison of the n.m.r. spectrum obtained for the compound prepared by Horton and his co-workers[4] * with that of our 2-phenylazo-analogue (2) permitted the *allo*-configuration to be assigned to the latter. The most

TABLE 1

N.m.r. parameters (τ values; J in Hz) for methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-*C*-methylene-2-phenylazo-α-D-allopyranoside (2) in $CDCl_3$ measured at 100 MHz

H-3	H-4	H_X	H_N	H-6*eq*	H-6*ax* and -5
7·5(oct)	5·9(q)	8·3(q)	7·94(q)	5·6(q)	6·25—6·42
$J_{3,X}$ 9 $J_{3,N}$ 7 $J_{3,4}$ 5	$J_{4,5}$ 9 $J_{4,3}$ 5	$J_{X,3}$ 9 $J_{X,N}$ 5·5	$J_{N,3}$ 7 $J_{N,X}$ 5·5	$J_{6eq,6ax}$ 8·5 $J_{6eq,5}$ 3·5	
(oct)	(q)	(q)	(q)	Irrad.	Collapse
(q) J 9 and 7	Irrad.	(q)	(q)		
Irrad.	(d) J 9	(d) J 5·5	(d) J 5·5		

The following signals were also present: Ph_2 2·3—2·8 (complex m); PhC*H*, 4·42(s); MeO, 6·5(s); H-1, 3·88(s).

significant similarity between the two spectra was the identical $J_{3,4}$ value of 5 Hz that they exhibited. Furthermore, the structurally related 2,3-epoxy-, 2,3-epithio-, and 2,3-epimino-derivatives of methyl 4,6-*O*-benzylidene-α-D-glycopyranoside with the *allo*-configuration exhibited a $J_{3,4}$ value in the range 4·5—5·0 Hz, whereas $J_{3,4}$ was zero for the *manno*-isomers.[7] The methylene cyclopropane protons H_X and H_N in the phenylazo-compound (2), have been assigned to the *exo*- and *endo*-positions respectively. The *exo*-proton would be expected to be

* We thank these authors for permitting us to see an unpublished spectrum.

[1] Part I, P. M. Collins, D. Gardiner, S. Kumar, and W. G. Overend, preceding paper.

[2] Preliminary report, P. M. Collins, D. Gardiner, S. Kumar, and W. G. Overend, *Chem. Comm.*, 1970, 1433.

[3] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1353.

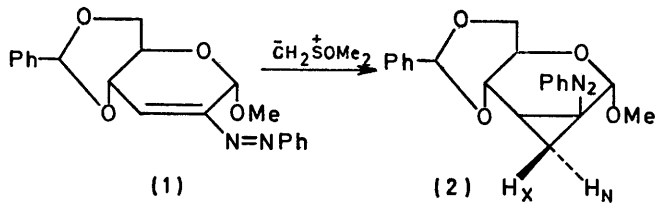
[4] E. L. Albano, D. Horton, and J. H. Lauterbauch, *Chem. Comm.*, 1968, 357; *Carbohydrate Res.*, 1969, **9**, 149.

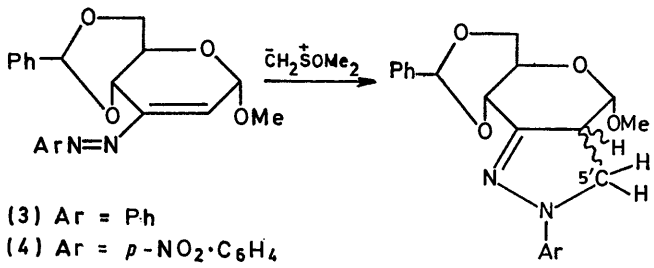
[5] B. Fraser-Reid and B. Radatus, *Canad. J. Chem.*, 1970, **48**, 2146.

[6] W. Meyer zu Reckendorf and U. Kamprath-Scholtz, *Angew. Chem. Internat. Edn.*, 1968, **7**, 142; J. S. Brimacombe, M. E. Evans, E. J. Forbes, A. B. Foster, and J. M. Webber, *Carbohydrate Res.*, 1967, **4**, 239; D. Horton and C. G. Tindall, jun., *Carbohydrate Res.*, 1970, **15**, 215.

[7] D. H. Buss, L. Hough, L. D. Hall, and J. F. Manville, *Tetrahedron*, 1965, **21**, 69.

more strongly coupled to H-3, with which it has a *cis*-relationship, than the *endo*-proton, which is *trans* [8] to H-3.





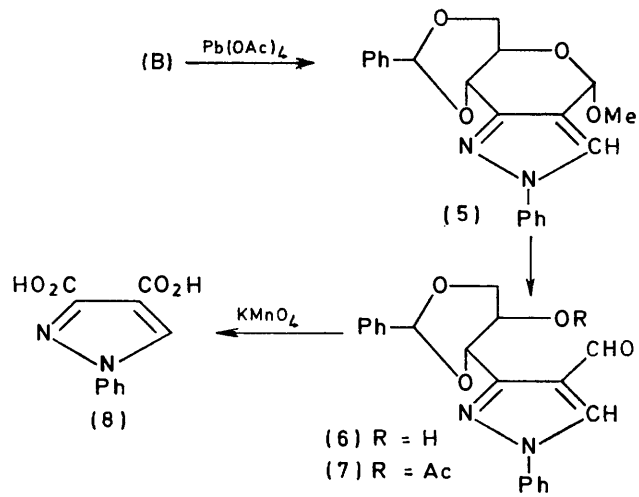
(3) Ar = Ph
(4) Ar = p-NO_2·C_6H_4

(A) and (B) Ar = Ph
(B′) Ar = p-NO_2·C_6H_4

In the same way the 3-phenylazo-derivative (3) was treated with the ylide and two compounds, (A) and (B), were produced. From one experiment a pure sample of compound (A) was isolated from the product mixture, and from a repeat experiment a pure sample of (B) was obtained. The molecular formula, which was the same for both compounds, indicated that they had been formed by the addition of a methylene residue to the starting material, but neither isomer (A) nor (B) appeared to possess either a cyclopropane ring or a phenylazo-grouping. The i.r. and u.v. spectra indicated the presence of a C=N–NPh unit. Further, the i.r. spectra showed the absence of >N–H residues, and this was substantiated by the n.m.r. spectra. The n.m.r. spectra further suggested that the compounds were isomeric and that the methylene group had added to the azoalkene system to afford the 1′-phenyl-$\Delta^{2'}$-pyrazoline derivatives (A) and (B).

The presence of the five-membered ring containing nitrogen was proved by the following oxidative degradation sequence. Compound (B) was dehydrogenated with lead tetra-acetate [9] in glacial acetic acid to afford two products. One of these had a molecular formula which showed that its formation from compound (B) simply involved the loss of a molecule of hydrogen. Thus the product could be the pyrazole derivative (5), an assignment confirmed by the u.v.[10] and i.r. spectra.[11] The n.m.r. spectrum showed a characteristic [12] low-field singlet for the pyrazole ring proton. The anomeric proton signal was at much lower field than is usual for a simple pyranoside derivative, but its chemical shift was reasonable for an anomeric proton which was also in a position α to a pyrazole ring. Signals for the four other ring protons were all present in the 60 MHz spectrum at reasonable chemical shifts but they were not amenable to first-order analysis.

The other product formed was also a pyrazole derivative, as shown by the spectroscopic evidence, but the data further indicated that the glycoside had suffered hydrolysis as well as dehydrogenation. For example, the n.m.r. spectrum possessed no signal for the aglycone methyl group, but a highly characteristic signal for an aldehydic proton was present. This indicated that the product existed in the open chain form (6), a conclusion supported by the presence of a hydroxy-proton signal. Analysis of the four other chain proton signals was not feasible at the field strength used to measure the spectrum, but acetylation of the free alcoholic group, gave a product (7) whose spectrum could be completely analysed. The u.v. absorption maxima of the acylic compounds (6) and (7) were bathochromically shifted compared with that of the cyclic derivative (5). This would be expected for a system in which a pyrazole ring was conjugated with an aldehydic group. The i.r. spectra of compounds (6) and (7) showed absorptions for a pyrazole ring and a conjugated carbonyl group. The acyclic pyrazole (6) could be formed from the glycoside derivative (5) by treatment of the latter with glacial acetic acid. A discussion of a



possible mechanism for this ring-opening reaction has been reported elsewhere.[13]

The glycosidically substituted pyrazole derivative (5) was unaffected by potassium permanganate, but the acyclic derivative (6) was oxidised readily with this reagent to give the known [14] 1-phenylpyrazole-3,4-dicarb-

[8] D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1963, **85**, 3218; H. M. Hutton and T. Schaefer, *Canad. J. Chem.*, 1963, **41**, 2774; S. Meiboon and L. C. Snyder, *J. Amer. Chem. Soc.*, 1967, **89**, 1038.

[9] G. F. Duffin and J. D. Kendall, *J. Chem. Soc.*, 1954, 408.

[10] A. N. Kost and I. I. Grandberg, *Adv. Heterocyclic Chem.*, 1966, **6**, 347.

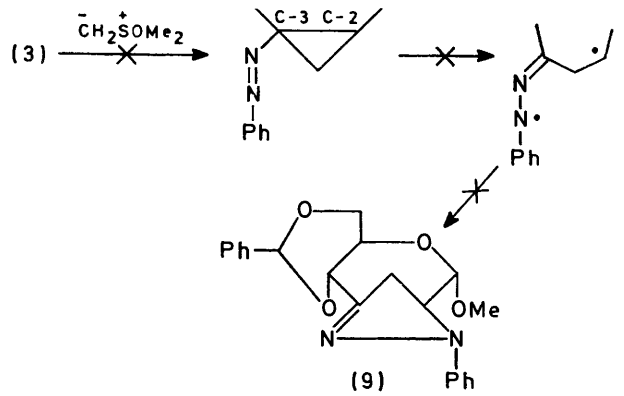
[11] A. R. Katritzky and A. P. Ambler in ' Physical Methods in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, London, 1963, vol. 2, p. 103.

[12] J. K. Williams, *J. Org. Chem.*, 1964, **29**, 1377.

[13] P. M. Collins, S. Kumar, and W. G. Overend, *Carbohydrate Res.*, 1972, **22**, 187.

[14] J. H. Birkinshaw, A. E. Oxford, and H. Raistrick, *Biochem. J.*, 1936, **30**, 394.

oxylic acid (8). This degradative sequence proves that a 1′-phenyl-$\Delta^{2'}$-pyrazoline ring was present in the original material, and excludes a product with structure (9), since this would yield 1-phenylpyrazole-3,5-dicarboxylic acid.[15] A product with the ring-expanded structure (9) requires consideration because it could have arisen by a rearrangement of an initially formed cyclopropane



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derivative (Scheme). Examples of interconversion between azocyclopropane derivatives and pyrazolines of this type are known.[16]

The n.m.r. spectra of isomers (A) and (B) indicated boat-like conformation, thereby increasing the dihedral angle between H-1 and H-2. This would probably give rise to a $J_{1,2}$ value larger than 4 Hz. The 220 MHz spectrum of isomer (B) could be analysed, with the aid of double-resonance studies carried out at 100 MHz, by a first-order treatment. The results are in Table 2. The spectrum of isomer (A), however, was not so well resolved; several protons had the same chemical shifts. However, the H-1 doublet could be clearly seen. Since isomer (A) has a $J_{1,2}$ value of 4·5 Hz, which is smaller than that of 5·5 Hz observed for isomer (B), the former can be tentatively assigned the *ribo*-structure and the latter the *arabino*-structure.

The *p*-nitrophenylazo-compound (4) likewise formed a pyrazoline derivative. The isomer isolated (B′) appears to have the same stereochemistry as (B), since the two compounds gave 60 MHz n.m.r. spectra that were virtually identical over the whole range scanned, except for the aromatic region.

The product isolated from the reaction of dimethylsulphoxonium methylide with the β-anomer (10) of the 3-phenylazo-compound again showed none of the spectral features expected for a cyclopropane derivative. However, the results were consistent with the product being the pyrazoline derivative (11). The evidence available did not permit an assignment of configuration at C-2.

The results of these ylide additions show that there is a

TABLE 2

N.m.r. parameters (τ values; J in Hz) for 1′-phenyl(methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-hexopyranosido [3,2-*c*]-$\Delta^{2'}$-pyrazoline [isomer (B)] in $CDCl_3$–C_6D_6 (5 : 1)

(a) At 220 MHz

H-4	H-1	H-6*eq*	H-5	H-5′	H-6*ax*	H-2	H-5′
5·76(q)	5·78(d)	5·81(q)	6·4(sex)	6·39(q)	6·48(t)	6·77(t of q)	7·12(q)
$J_{4,5}$ 10	$J_{1,2}$ 5·5	$J_{6eq,6ax}$ 10	$J_{5,6ax}$ 10	$J_{5',2}$ 12	$J_{6ax,6eq}$ 10	$J_{2,5'}$ 12·0	$J_{5',2}$ 12
$J_{4,2}$ 2·5		$J_{6eq,5}$ 5	$J_{5,6eq}$ 5	$J_{5',5'}$ 10	$J_{6ax,5}$ 10	$J_{2,5'}$ 12·0	$J_{5',5'}$ 10
			$J_{5,4}$ 10			$J_{2,1}$ 5·5	
						$J_{2,4}$ 2·5	

(b) At 100 MHz

← Irrad. →				(q)	Unresolved	(t)	(q)
						J 12·0, 12	
(q)	(d)	(q)	(sex)	(d)	(t)	(d of q)	Irrad.
				J 12		J 12, 5·5, 2·5	

The following signals were also present: Ph_2 2·4—3·2; PhC*H*, 4·6; MeO, 6·87.

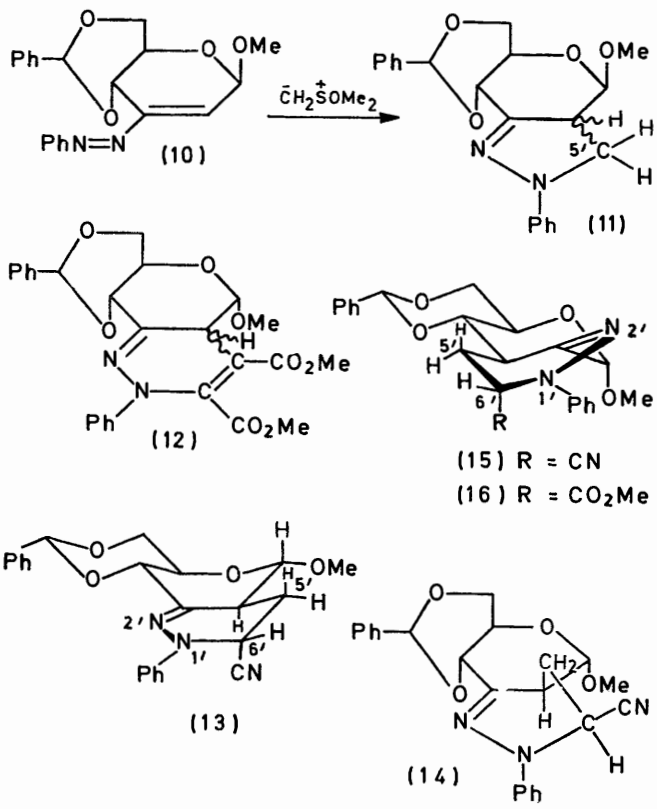
that they only differ in stereochemistry at position 2 of the pyranoid ring. Therefore, one isomer has the *ribo*-structure and the other the *arabino*-configuration. Molecular models indicated that a pyrazoline ring could be fused to the 2- and 3-positions of a pyranoid ring [as shown in (A) and (B)] in the *ribo*-configuration with little distortion to the latter system. Thus, in such a glycopyranoside the dihedral angle between the equatorial proton at H-1 and the axial proton at H-2 is normal and a coupling in the range 2—4 Hz would be expected. Fusion at C-2, in the opposite sense, to give the *arabino*-isomer, tends to distort the pyranoside system into a similarity between the reaction of dimethylsulphoxonium methylide with the azoalkene system in the 2-phenylazo-derivative (1), and with an enone system.[3] In both cases a methylene residue is inserted onto the carbon–carbon double bond. However, with the 3-phenylazo-derivatives (3), (4), and (10) used in this work, this ylide added in a 1,4-manner across the azoalkene system in the molecules. This mode of addition is uncommon with enones; 1,2-additions usually occur, either as already described or to the carbonyl group, to give epoxides. To our knowledge the only example of a sulphur ylide giving 1,4-addition across an enone system is in the

[15] H. El Khadem and M. M. Mohammed-Aly, *J. Chem. Soc.*, 1963, 4929.

[16] H. J. Rosenkranz and H. Schmid, *Helv. Chim. Acta*, 1968, **51**, 1628.

formation of a 2,3-dihydrofuran derivative from 3-ethylidenepentane-2,4-dione with (dimethylsulphonium ethoxycarbonylmethylide.[17]

The reason for the change in the mode of addition of this reagent to the 2- and the 3-phenylazo-derivatives is not yet clear. We made a suggestion earlier [2] that electronic effects are responsible for the difference, but further work is necessary to clarify this point.



Prolonged heating of solutions of the 3-phenylazohex-2-enopyranoside (3) gave a yellow crystalline product, the n.m.r. spectrum of which indicated that it was a Diels–Alder dimer. It appears that a carbon–carbon double bond of one molecule acted as the dienophile in this reaction, since this mode of addition would give rise to a yellow phenylazo-product. Such a dimerisation has been proposed for simple acyclic phenylazoalkenes.[18] There is a similarity between this reaction and the dimerisation that certain carbohydrate enones undergo.[19] In view of the ready dimerisation of this carbohydrate azoalkene derivative, it is strange that Diels–Alder additions to azoalkenes were a neglected route to tetrahydropyridazine derivatives [20] until the recent work of Caglioti *et al.*[21]

We have found that dienophiles add readily to the azoalkene unit in these derivatives. Dimethyl acetylenedicarboxylate, for example, gives a product which has been shown by spectroscopic methods to be a dihydropyridazine derivative. The structure of this adduct should be one of the easiest to determine, since undefined stereoisomerism can only occur at position 2 in the pyranoid ring [see (12)]. Although the coupling between H-1 and H-2 could be measured for this compound it was inadequate evidence upon which to base the stereochemistry at C-2. Failure to make this assignment arose because molecular models of the *ribo*- and the *arabino*-compounds showed that the dihedral angles between H-1 and H-2 in each compound were such that both could be expected to give the observed coupling constant.[22]

Acrylonitrile was added to the methyl phenylazohex-2-enopyranoside (3) and two products (P) and (Q) were isolated; spectroscopic evidence showed they were Diels–Alder adducts. Assignment of structures to these materials is complicated since orientational isomerism is possible in addition to configurational isomerism at two carbon atoms. In the n.m.r. spectrum (Table 3) of isomer (P) (which was isolated in the largest quantity) the signals for all the protons that are required for a structural determination are visible. The assignment of these protons has been confirmed by double-resonance studies. Because the H-6′ signal is a quartet, which is not coupled to H-2, it can be deduced that the terminal methylene carbon atom of the acrylonitrile must be attached to C-2 of the pyranoid ring and the carbon atom bearing the cyano-group to the nitrogen atom. Two further problems remain: the stereochemistry at C-6′ and that at C-2. The most reasonable assignment appears to be ring fusion to give the *arabino*-configuration for the sugar and the *R*-configuration at C-6′. An isomer with such a structure would most probably adopt the distorted conformation shown in (13). This molecular geometry would be expected [22] to give two small couplings between the equatorial H-6′ and the two protons at C-5′, and a large and a small coupling between the axial proton at C-2 and H-5′ (axial) and H-5′ (equatorial), respectively. The J values measured from the spectrum are in agreement with these predictions. The dihedral angle between H-1 and H-2, measured from a molecular model of a compound with structure (13), is *ca.* 180°. Thus the value of $J_{1,2}$ (7·5 Hz) observed is reasonable for the structure proposed for compound (P).

The *ribo*-configuration with the *R*-stereochemistry at C-6′ is a possible alternative structure for this compound. If the pyranoid ring and the tetrahydropyridazine ring of such an isomer both adopted a chair-like conformation, the dihedral angles between the protons at C-5′ and H-6′ and H-2 would all be in agreement with the measured coupling constants.[22] However, examination

[17] G. B. Payne, *J. Org. Chem.*, 1967, **32**, 3351.
[18] D. Y. Curtin and E. W. Tristam, *J. Amer. Chem. Soc.*, 1950, **72**, 5238.
[19] T. D. Inch and P. Rich, *Carbohydrate Res.*, 1968, **6**, 244.
[20] M. Lora-Tamayo and J. L. Soto, in '1,4-Cycloaddition Reactions,' ed. J. Hamer, Academic Press, New York, 1967, 179.
[21] L. Caglioti, G. Rosini, P. Tundo, and A. Vigevani, *Tetrahedron Letters*, 1970, 2349; L. Caglioti, G. Dondoni, and G. Rosini, *Chimica e Industria*, 1968, **50**, 122.
[22] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

of a molecular model of this isomer in this conformation showed that the dihedral angle between H-1 and H-2 was about 60° and this would probably give a smaller $J_{1,2}$ value than the value observed.[22] Therefore, of the two possible structures for compound (P), the isomer shown as (13), possessing the *arabino*-pyranoid ring and the *R*-configuration in the tetrahydropyridazine ring, appears more likely.

The n.m.r. spectrum of the other product (Q) has been analysed with the aid of double-resonance measurements (Table 3). The spectral parameters clearly indicate that (Q) is not a structural isomer of (P) but a stereoisomer, as shown in (14). The assignment was deduced from the multiplicity of the H-2 signal. This proton was shown to be coupled to three others, one of which was H-1 and the other two were the C-5′ methylene protons. Support for the structural assignment comes from the appearance of the H-6′ signal as a triplet, which showed that it was coupled only to the C-5′ methylene protons and not to H-2 as well. The $J_{1,2}$ value (8 Hz) for this isomer is large; therefore, it must also have the *arabino*-structure. Consequently, compounds (P) and (Q) are C-6′ isomers and (Q) must have the *S*-configuration at C-6′ as shown in (14). Unfortunately, this cannot be verified from the couplings between the C-5′ methylene protons and H-6′ because these *J* values cannot be determined from the deceptively simple spectrum obtained. This simplification arises because the C-5′ methylene protons fortuitously have coincident chemical shifts.

Acrylonitrile was also added to methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-α-D-*erythro*-hex-2-enopyranoside (1), to give two isomeric Diels–Alder addition products (X) and (Y). The n.m.r. parameters for the major isomer (X) are given in Table 4. Since the protons at C-5′ are both coupled vicinally to two protons, rather than one, and H-6′ is vicinally coupled to two protons, rather than three, then the methylene group of the tetrahydropyridazine ring must be attached to C-3 of the pyranoid ring. The stereochemistry at this carbon atom can be ascertained from the size of the vicinal couplings between the proton attached to C-3 and those at C-4 and C-5′. They clearly indicate that the substituted pyranoid ring has the *arabino*-configuration. The couplings between the proton at C-6′ and those at C-5′ indicate the *S*-configuration at the carbon atom in the tetrahydropyridazine ring with the cyano-group adopting an axial orientation as shown in (15). Thus, there is a close similarity between the structure of this isomer and that of the major product (13) obtained from the 3-phenylazohex-2-enopyranoside with acrylonitrile. The n.m.r. spectrum of the minor product (Y) was not sufficiently well resolved to allow a stereochemical or orientational assignment to be made.

The 2-phenylazo-compound (1) reacted with methyl acrylate to afford two products. Only one was isolated

TABLE 3

N.m.r. parameters (τ values; *J* in Hz) for compounds (P) and (Q) measured at 100 MHz

H-1	H-2	H-5′*eq*	H-5′*ax*	H-6′	H-4, -5, -6*ax*, and -6*eq*
Compound (P) in $CDCl_3$ *					
5·43(d)	6·76(cm)	7·43(oct)	7·92(sex)	5·09(q)	5·45—6·3
$J_{1,2}$ 7·5	$J_{2,5'ax}$ 12	$J_{5'eq,5'ax}$ 13	$J_{5'ax,5'eq}$ 13	$J_{6',5'ax}$ 4·5	
	$J_{2,5'eq}$ 7	$J_{5'eq,2}$ 7	$J_{5'ax,2}$ 12	$J_{6',5'eq}$ 2·5	
	$J_{2,1}$ 7·5	$J_{5'eq,6'}$ 2·5	$J_{5'ax,6'}$ 4·5		
(d)	(cm)	(q) *J* 13, 7	(t) *J* 13, 12	Irrad.	Unchanged
(s)	Irrad.	(q) *J* 13, 2·5	(q) *J* 13, 4·5	(q)	Unchanged
Irrad.	(q) *J* 12, 7	(oct)	(sex)	(q)	Unchanged
Compound (Q) in C_6D_6 *					
5·19(d)	7·55br(q)	8·25br(t)	8·25br(t)	6·60(t)	5·7—6·0 (cm, 3H) 6·3 — 6·6 (cm, 1H)
$J_{1,2}$ 8	$J_{2,1}$ 8	$J_{5',2}$ 6	$J_{5',2}$ 6		
	$J_{2,5'}$ 6 †	$J_{5',6'}$ 4 †	$J_{5',6'}$ 4 †		
	$J_{2,5'}$ 6 †				
Irrad.	(t) *J* 6·0, 6·0	br(t)	br(t)	(t)	Unchanged
(s)	Irrad.	br(d) *J* 4·0	br(d) *J* 4·0	(t)	Unchanged
(d)	br(q)	(d) *J* 6·0	(d) *J* 6·0	Irrad.	—
(d)	br(q)	br(t)	br(t)	(t)	Irrad. at 6·45

cm = Complex m.

* Signals for Ph_2, PhC*H*, and MeO appeared at the expected chemical shifts. † These values are half the sum of two unequal *J*'s.

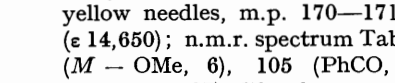
and it was found to be the tetrahydropyridazine derivative, from its n.m.r. spectrum (Table 4). This adduct (16) has the same stereochemistry as the major product formed by addition of acrylonitrile to compound (1).

Methyl acrylate also reacted with the 3-phenylazohex-2-enopyranoside (3) and two products were isolated. The n.m.r. spectra, which were measured at 60 MHz, showed that they were Diels–Alder adducts, but the signals were insufficiently resolved to permit stereochemical assignments to be made.

EXPERIMENTAL

Unless stated otherwise spectroscopic and optical rotation measurements were made as in the preceding paper. The n.m.r. spectra obtained at 220 MHz were measured on a Varian HR 200 spectrometer. T.l.c. was carried out on silica with benzene–ethyl acetate (4 : 1) as developer; compounds were located with anisaldehyde–sulphuric acid.

Addition of Dimethylsulphoxonium Methylide to Methyl 4,6-O-*Benzylidene*-2,3-*dideoxy*-2 (or 3)-*phenylazo*-D-*hex*-2-*enopyranosides*.—(a) *Methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-2,3-C-*methylene*-2-*phenylazo*-α-D-*allopyranoside* (2). Dimethylsulphoxonium methylide was prepared by stirring trimethylsulphoxonium iodide (0·28 g, 1·3 mmol) with sodium hydride (0·026 g, 1·1 mmol) in anhydrous dimethyl sulphoxide (10 ml) under dry nitrogen until the evolution of hydrogen ceased (usually 1 h). Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-α-D-*erythro*-hex-2-enopyranoside (1) (0·35 g, 1 mmol) was then added and, after a further 10 min stirring, the reaction was quenched with ice–water (50 ml). The yellow solid which precipitated was collected and recrystallised from ethanol to afford the 2,3-C-*methylene*-2-*phenylazo-derivative* (2) (0·25 g, 60%) as fine yellow needles, m.p. 170—171, $[\alpha]_D$ +101°, $\lambda_{max.}$ 278 nm (ε 14,650); n.m.r. spectrum Table 1; *m/e* 366 (M^+, 6%), 335 (M − OMe, 6), 105 (PhCO, 35), 91 (C_7H_7, 35), and 77 (C_6H_5, 97) [the base peak, *m/e* 217 could be the



ion (where R = N_2Ph) formed by *h* rupture [23] (Found: C, 68·6; H, 6·1; N, 7·4. $C_{21}H_{22}N_2O_4$ requires C, 68·8; H, 6·1; N, 7·7%).

(b) 1′-*Phenyl*[*methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-α-D-arabino(*or* ribo)-*hexopyranosido*][3,2-c]-$\Delta^{2'}$-*pyrazoline*. The methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-α-D-hex-2-enopyranoside (3) (4·1 g, 11 mmol) was treated as in (a) with trimethylsulphoxonium iodide (3·0 g, 14 mmol) and sodium hydride (0·3, 13 mmol) in dimethyl sulphoxide (60 ml). After work-up in the usual manner and recrystallisation from ethanol, fine white needles (2·6 g) were obtained which were shown by t.l.c. analysis to be composed of two compounds (A) and (B). The more mobile *material* (B) preponderated and after further recrystallisation from ethanol it was isolated in a chromatographically pure state (1·9 g), m.p. 150—151°, $[\alpha]_D$ −317°, $\lambda_{max.}$ 294 (ε 19,640) and 242 nm (14,580), $\nu_{max.}$ 1600 and 1500 (Ph–N–N=C<) cm^{-1}; n.m.r. data in Table 2; *m/e* 366 (M^+, 23%), 171(100), 105 (PhCO, 23), 91 (C_7H_7, 26), and 77 (C_6H_5, 44) (Found: C, 68·7; H, 6·2; N, 7·2. $C_{21}H_{22}N_2O_4$ requires C, 68·8; H, 6·1; N, 7·7%).

TABLE 4

N.m.r. parameters (τ values; J in Hz) for compounds (X) and (16) measured at 100 MHz in $CDCl_3$

Cyano-derivative (X) *

H-1	H-3	H-5′*eq*	H-5′*ax*	H-6′	H-4	-5, -6*eq*, -6*ax*
4·7(d)	6·66(oct)	7·49(oct)	7·92(sex)	5·19(q)		5·4—6·4
J 1·5	$J_{3,5'ax}$ 13	$J_{5'ag,5'ax}$ 13	$J_{5'ax,5'eq}$ 13	$J_{6',5'ax}$ 5		
	$J_{3,5'eq}$ 5	$J_{5'eq,3}$ 5	$J_{5'ax,3}$ 13	$J_{6',5'eq}$ 2		
	$J_{3,4}$ 9·5	$J_{5'eq,6'}$ 2	$J_{5'ax,6'}$ 5			
(d)	(oct)	(q) J 13, 5	(t) J 13, 13	Irrad.		

Methoxycarbonyl derivative (16) †

4·68(d)	6·98(oct)	7·48(oct)	8·00(sex)	5·37(q)	5·92(t)	6·1—6·6 (cm)	5·62(q)
J 1·5	$J_{3,5'ax}$ 13·5	$J_{5'eq,5'ax}$ 13·5	$J_{5'ax,5'eq}$ 13·5	$J_{6',5'ax}$ 6	$J_{4,3}$ 9		$J_{6,6}$ 15·5
	$J_{3,5'eq}$ 5	$J_{5'eq,3}$ 5	$J_{5'ax,3}$ 13·5	$J_{6',5'eq}$ 1·5	$J_{4,5}$ 9		$J_{6,5}$ 10·5
	$J_{3,4}$ 9	$J_{5'eq,6'}$ 1·5	$J_{5'ax,6'}$ 6				

cm = Complex m.

* The following signals were also present: Ph_2 2·5—3·2 (cm); PhC*H*, 4·48(s); MeO, 6·48(s). † The following signals were also present: Ph_2, 2·4—3·3 (cm); PhC*H*, 4·50(s); MeO, 6·25(s); MeO, 6·46(s).

When this experiment was repeated under similar conditions the first crop of crystals, obtained in 35% yield, was composed mainly of compound (A), which had a lower t.l.c. mobility. After two recrystallisations a chromatographically homogeneous sample of *isomer* (A) was obtained, m.p. 221—223°, $[\alpha]_D$ +224°, $\nu_{max.}$ 1600 and 1500 cm^{-1} (Ph–N–N=C), τ (220 MHz; $CDCl_3$) 2·3—3·3 (complex m, 10H, Ph_2), 4·53 (s, 1H, PhC*H*), 5·55 (d, $J_{1,2}$ 4·5 Hz, 1H, H-1), 5·87 (complex m, 2H), 6·15 (complex m, 1H), 6·36 (t, J 10 and 10 Hz, 1H), 6·56 (complex m, 2H), 7·0 (complex m, 1H), and 7·0 (s, 3H, OMe) (double-resonance studies at 100 MHz were of little help in analysing this spectrum) (Found: C, 69·1; H, 6·05; N, 7·9%).

(c) 1′-*Phenyl*[*methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-β-D-arabino(*or* ribo)-*hexopyranosido*][3,2-c]-$\Delta^{2'}$-*pyrazoline* (11). The 3-phenylazo-β-D-*erythro*-hex-2-enopyranoside (10) (0·35 g) was treated as described in (b). The white solid obtained on addition of water was composed of two products. However, recrystallisation (thrice) from ethanol yielded a white, chromatographically homogeneous sample of the major *component* (11) (0·16 g, 44%), m.p. 230—232°, $[\alpha]_D$ −258°, $\lambda_{max.}$ 292 (ε 34,220) and 242 nm (24,880), $\nu_{max.}$ 1600 and 1500 cm^{-1}; τ (60 MHz; $CDCl_3$) 2·2—3·2 (complex m, 10H, Ph_2), 4·3 (s, 1H, PhC*H*), 5·4—6·4 (complex m, 6H), 6·45 (s, 3H, OMe), and 6·5—6·8 (complex m, 2H); *m/e* 366 (M^+, 48%), 171(100), 105(13), 91(19), and 77(22)

[23] O. S. Chizhov, L. S. Golovkina, and N. S. Wulfson, *Carbohydrate Res.*, 1968, **6**, 138.

(Found: C, 68·7; H, 6·0; N, 7·7. $C_{21}H_{22}N_2O_4$ requires C, 68·8; H, 6·1; N, 7·7%).

(d) 1′-p-*Nitrophenyl*[*methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-α-D-arabino(*or* ribo)-*hexopyranosido*][3,2-c]-$\Delta^{2'}$-*pyrazoline* (B). Trimethylsulphoxonium chloride (0·08 g) was dissolved in anhydrous tetrahydrofuran (15 ml), sodium hydride (0·013 g) was added, and the mixture was heated at 60° for 1·5 h. The 3-*p*-nitrophenylazo-hexenopyranoside (4) (0·2 g) in tetrahydrofuran (10 ml) was then added and heating at 50° was continued for 30 min. The usual work-up afforded a product composed of three compounds. The major component was the most mobile (t.l.c.). This material was isolated by p.l.c. and recrystallised from ethanol to give the 1′-p-*nitrophenyl*-$\Delta^{2'}$-*pyrazoline derivative* (B′) as yellow needles (0·05 g, 24%), m.p. 249—250°, $[\alpha]_D$ −575°, $\nu_{max.}$ 1600 and 1500 (Ph–N–N=C<) and 1520 cm^{-1} (NO_2), τ (60 MHz; $CDCl_3$) 1·8—3·1 (complex m, 9H, Ph, Ar), 4·25 (s, 1H, PhC*H*), 5·1—6·4 (complex m, 8H), and 6·5 (s, 3H, OMe), *m/e* 411 (M^+, 10%), 216(100), 149(17), 105(27), 91(30), and 77(27) (Found: C, 61·2; H, 5·3; N, 9·8. $C_{21}H_{21}N_3O_6$ requires C, 61·3; H, 5·2; 10·2%). The minor products from this reaction were not isolated.

Oxidation of the Pyranosidopyrazoline (B).—(a) *With potassium permanganate.* Isomer (B) (0·5 g), dissolved in 50% aqueous acetone (10 ml) containing potassium carbonate (0·1 g), was mixed with an aqueous solution (20 ml) of potassium permanganate (0·5 g) with vigorous stirring. The mixture was heated under reflux for 2 h and the manganese dioxide which precipitated was filtered off and washed with water. The combined aqueous solutions were evaporated, acidified, and extracted with methylene chloride. After washing with water the extract was concentrated to give a crystalline residue (0·04 g), m.p. 119—121°, identical (mixed m.p.) with benzoic acid.

(b) *With lead tetra-acetate.* To a cooled solution of the pyrazoline derivative (B) (2·6 g) in glacial acetic acid (2·5 ml), lead tetra-acetate (3·8 g) was added. The mixture was shaken vigorously for 30 h, diluted with water (*ca.* 25 ml) and cooled. The yellow solid that separated was shown (t.l.c.) to be composed of two compounds. These were separated by column chromatography on silica gel with benzene–ethyl acetate (4 : 1) as eluant. The more mobile component was 1′-*phenyl*(*methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-α-D-erythro-*hexopyranosido*)[3,2-c]*pyrazole* (5) (0·45 g, 17%), m.p. 185—187°, $[\alpha]_D$ −57° (*c* 0·3 in EtOH), $\lambda_{max.}$ 260 nm (ε 16,870), $\nu_{max.}$ 1590, 1570, and 1480 cm^{-1} (pyrazole ring), τ (60 MHz; $CDCl_3$) 2·05 (s, 1H, pyrazole ring), 2·15—2·7 (complex m, 10H, Ph_2), 4·15 (s, 1H, H-1), 4·3 (s, 1H, PhC*H*), 5·09 (q, *J* 6 and 3 Hz, 1H), 5·4—6·1 (complex m, 3H), and 6·43 (s, 3H, OMe) (Found: C, 69·4; H, 5·5; N, 7·7. $C_{21}H_{20}N_2O_4$ requires C, 69·2; H, 5·4; N, 7·7%).

The more polar component was removed from the column with ethyl acetate and recrystallised from ethanol to give 1-*phenyl*-3-(1,3-O-*benzylidene*-D-erythro-*glyceryl*)*pyrazole*-4-*carbaldehyde* (6) (0·75 g, 30%), m.p. 172—174°, $[\alpha]_D$ −6°, $\lambda_{max.}$ 272 nm (ε 17,520), $\nu_{max.}$ 3320 (OH), 1660 (CHO conj.), 1600, 1530, and 1500 cm^{-1} (pyrazole ring), τ (60 MHz; $CDCl_3$) −0·4 (s, 1H, CHO), 1·4 (s, 1H, pyrazole ring), 2·15—2·7 (complex m, 10H, Ph_2), 4·2 (s, 1H, PhC*H*), 4·7—6·15 (complex m, 4H), and 6·67br (m, 1H, OH, exchangeable with D_2O) (Found: C, 68·3; H, 5·2; N, 8·0. $C_{20}H_{18}N_2O_4$ requires C, 68·6; H, 5·2; N, 8·0%).

Oxidation of Compounds (5) *and* (6) *with Potassium Permanganate.*—(*a*) To a mixture of compounds (5) and (6) (0·4 g) in pure acetone (10 ml) were added during 2 days with vigorous stirring, potassium permanganate (0·6 g) and potassium carbonate (0·1 g). The mixture was acidified with dilute hydrochloric acid and then sodium disulphite was added until the manganese dioxide dissolved. The mixture was then diluted with water (50 ml) and extracted with methylene chloride (2 × 30 ml); the extract was washed with water, dried, and evaporated to give a solid. On trituration with ether this yielded pure crystalline 1-phenylpyrazole-3,4-dicarboxylic acid (8) (0·04 g), m.p. 230—231° (decomp.) (lit.,[14] 232°), $\lambda_{max.}$ 262 nm (ε 10,530), titrimetric equiv. wt. 120·9 (calc. 116·1) (Found: C, 56·7; H, 3·5; N, 12·0. Calc. for $C_{11}H_8N_2O_4$: C, 56·9; H, 3·5; N, 12·1%).

(*b*) The pyrazole derivative (6) (0·1 g) was treated as described in (*a*). After 30 h, t.l.c. revealed that all the starting material had been consumed. The usual work-up afforded 1-phenylpyrazole-3,4-dicarboxylic acid (8) (0·015 g, 23%), m.p. 230—231°.

(*c*) When compound (5) (0·1 g) was treated as described in (*a*) only starting material could be detected (t.l.c.) in the mixture after 3 days.

Treatment of Compound (5) *with Acetic Acid.*—Treatment of compound (5) (0·2 g) with glacial acetic acid (2 ml) at room temperature converted it into the less mobile acyclic pyrazole derivative (6). This conversion was complete in 24 h (t.l.c.). The product was extracted into methylene chloride (2 × 10 ml) and the solid finally obtained was recrystallised from ethanol to give material with m.p. 172—173°, identical (mixed m.p.) with compound (6).

Acetylation of the Pyrazole Derivative (6).—The pyrazole derivative (6) (0·2 g) was treated with acetic anhydride (0·3 ml) in anhydrous pyridine (1·5 ml) at room temperature for 2 h. The mixture was poured into ice–water and the white solid which separated was recrystallised from methylene chloride–light petroleum (b.p. 40—60°) to give the O-*acetyl derivative* (7) of compound (6) (0·21 g, 94%), m.p. 147—149°, $[\alpha]_D$ −13°, $\lambda_{max.}$ 271 nm (ε 13,840), $\nu_{max.}$ 1730 (ester C=O), 1610 (CHO conj.), 1595, 1525, and 1500 cm^{-1} (pyrazole). The 60 MHz n.m.r. spectra ($CDCl_3$ or C_6D_6) showed 20 protons. In $CDCl_3$ the low-field signals were resolved best: τ −0·5 (s, 1H, CHO), 1·4 (s, 1H, pyrazole ring), and 2·2—2·8 (complex m, 10H, Ph_2). The signals for the remaining 8 protons were more easily analysed in the spectrum measured in C_6D_6: τ 4·05 (sex, $J_{5,4}$ 10, $J_{5,6ax}$ 10, $J_{5,6eq}$ 5 Hz), 4·4 (s, H-3), 4·61 (d, $J_{4,5}$ 10 Hz), 5·51 (q, $J_{6eq,6ax}$ 10·5, $J_{6eq,5}$ 5 Hz), 6·4 (t, $J_{6ax,6eq}$ 10·5, $J_{6ax,5}$ 10 Hz), and 8·47 (s, 3H, AcO) (Found: C, 67·2; H, 5·3; N, 7·2. $C_{22}H_{20}N_2O_5$ requires C, 67·3; H, 5·1; N, 7·1%).

Diels–Alder Additions to Phenylazo-α-D-hex-2-enopyranoside Derivatives.—(a) 3-*Phenylazo derivatives.* (i) *Addition of dimethyl acetylenedicarboxylate.* The 3-phenylazohex-2-enopyranoside (3) (1·1 g) and dimethyl acetylenedicarboxylate (5·8 g) were heated together on a steam-bath for 1 h. T.l.c. revealed one major product. This was isolated by removing the excess of acetylenic ester under reduced pressure (1·33 Nm^{-2}) and subjecting the residue to column chromatography on silica gel. The major product, eluted with benzene–ethyl acetate (4 : 1), was *dimethyl* 1′,4′-*dihydro*-1′-*phenyl*(*methyl*-4,6-O-*benzylidene*-2,3-*dideoxy*-α-D-*hexopyranosido*)[3,2-c]*pyridazine*-5′,6′*dicarboxylate* (12) (0·92 g, 60%), m.p. 122—124°, $[\alpha]_D$ −101°, $\nu_{max.}$ 1750 and 1740 (ester C=O), and 1600 and 1500 cm^{-1} (Ph–N–N=C<), τ (60 MHz; $CDCl_3$) 2·3—3·2 (complex m, 10H, Ph_2), 4·33 (s,

1H, PhC*H*), 4·91 (d, $J_{1,2}$ 5·5 Hz), 5·75 (d, $J_{2,1}$ 5·5 Hz), 5·3—5·9 (complex m, 4H), 6·30 (s, 3H), 6·50 (s, 3H), and 6·58 (s, 3H, OMe).

(ii) *Addition of acrylonitrile.* The 3-phenylazohex-2-enopyranoside (3) (1·8 g) and acrylonitrile (50 ml) were mixed and stored in the dark at room temperature for 4 days. T.l.c. revealed that two substances, (P) and (Q), were present in the almost colourless solution. The less mobile material was the major component. The solution was concentrated under reduced pressure (1·33 N m^{-2}). This gave a solid residue which was recrystallised twice from methanol to afford a chromatographically homogeneous sample of the less mobile component (P), (6′ R)-*1′,4′,5′,6′-tetrahydro-1′-phenyl(methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-α-D-*hexopyranosido*)[3,2-c]*pyridazine*-6′-*carbonitrile* (13) (0·8 g, 38%), m.p. 221—223°, $[\alpha]_D$ −262°, $\nu_{max.}$ 1605 and 1505 cm^{-1} (Ph–N–N=C<, and 2236·5 cm^{-1} (Raman spec.) (C≡N); 100 MHz n.m.r. data in Table 3 (Found: C, 67·9; H, 6·2; N, 10·4. $C_{23}H_{23}N_3O_4$ requires C, 68·1; H, 5·7; N, 10·4%).

The mother liquors yielded a further crop of crystals which after recrystallisation (twice) afforded a chromatographically pure sample of the more mobile *isomer* (Q) (0·3 g, 15%) which was shown to have structure (14); m.p. 197—199°, $[\alpha]_D$ −350°; 100 MHz n.m.r. data (C_6D_6) in Table 3 (Found: C, 68·1; H, 5·7; N, 10·2%).

(iii) *Addition of methyl acrylate.* The 3-phenylazo-compound (3) (1·8 g) was treated with methyl acrylate (50 ml) as described for the acrylonitrile reaction. Although the solid (1·7 g) obtained appeared to be chromatographically homogeneous, i.r. and n.m.r. spectral evidence suggested otherwise. After recrystallisation from ethanol (seven times) a pure sample of one isomer of an *adduct* (the major product) was obtained with m.p. 183—186°, $[\alpha]_D$ −467°, $\nu_{max.}$ 1750 (ester C=O), and 1600 and 1500 cm^{-1} (Ph–N–N=C<), τ (60 MHz; $CDCl_3$) 2·3—3·3 (complex m, 10H, Ph_2), 4·32 (s, PhC*H*), 5·2—6·4 (complex m, 7H), 6·35 (s, 3H, OMe), 6·6 (s, 3H, OMe), and 6·8—8·0 (complex m, 2H) (Found: C, 65·5; H, 6·0; N, 6·3. $C_{24}H_{26}N_2O_6$ requires C, 65·7; H, 6·0; N, 6·4%).

After repeated recrystallisation of the material obtained from the mother liquor of the major compound, a small sample of a minor product was obtained with m.p. 227° (decomp.), $[\alpha]_D$ −239°, $\nu_{max.}$ 1740 (ester C=O), and 1600 and 1500 cm^{-1} (Ph–N–N=C<), τ (60 MHz; $CDCl_3$) 2·2—3·3 (complex m, 10H, Ph_2), 4·31 (s, PhC*H*), 5·2—6·0 (complex m, 7H), 6·37 (s, 3H, OMe), 6·60 (s, 3H, OMe), and 6·7—8·0 (complex m, 2H).

(b) *2-Phenylazo-derivatives.* (i) *Addition of acrylonitrile.* The 2-phenylazo-derivative (1) (0·5 g) was treated with acrylonitrile in an identical manner to that used for the 3-phenylazo-analogue. Two products, (X) and (Y), were formed. Recrystallisation of the crude mixture from ethanol afforded the major component (X) (0·26 g, 45%) which was shown to be (6′ S)-*1′,4′,5′,6′-tetrahydro-1′-phenyl-(methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-α-D-*hexopyranosido*)-[2,3-c]*pyridazine*-6′-*carbonitrile* (15), m.p. 202—203°, $[\alpha]_D$ −113°, $\lambda_{max.}$ 276 nm (ε 18,980), $\nu_{max.}$ 1600 and 1495 cm^{-1} (Ph–N–N=C<); see Table 4 for n.m.r. spectrum (100 MHz) (Found: C, 68·3; H, 5·9; N, 10·5. $C_{23}H_{23}N_3O_4$ requires C, 68·1; H, 5·7; N, 10·4%).

Recrystallisation of the residue obtained from the mother liquor of compound (X) gave a pure sample of *isomer* (Y) (0·18 g, 31%), m.p. 196—197° (decomp.), $[\alpha]_D$ −343°, $\lambda_{max.}$ 277 nm (ε 20,250), $\nu_{max.}$ 1600 and 1495 cm^{-1} (Ph–N–N=C<), τ (100 MHz; $CDCl_3$) 2·4—3·0 (complex m, 10H, Ph_2), 4·5 (s, PhC*H*), 4·95 (s, 1H, H-1), 5·3—6·5 (complex m, 6H), 6·56 (s, 3H, OMe), and 6·6—7·6 (complex m, 2H) (Found: C, 68·0; H, 5·7; N, 10·4%).

(ii) *Addition of methyl acrylate.* The 2-phenylazo-derivative (1) (0·35 g) was treated with the ester as described for the 3-phenylazo-isomer. This reaction afforded two products, one of which, (6′ S)-*methyl 1′,4′,5′,6′-tetrahydro-1′-phenyl(methyl* 4,6-O-*benzylidene*-2,3-*dideoxy* α-D-*hexopyranosido*)[2,3-c]-*pyridazine*-6′-*carboxylate* (16), was isolated by fractional crystallisation from ethanol (yield 0·18 g, 40%), m.p. 208—210°, $\nu_{max.}$ 1730 (ester C=O), 1580, 1570, and 1490 cm^{-1} (Ph–N–N=C<; n.m.r. data (100 MHz) in Table 4 (Found: C, 65·2; H, 6·1; N, 6·0. $C_{24}H_{26}N_2O_6$ requires C, 65·7; H, 6·0; N, 6·4%).

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